

USER'S GUIDE FOR POLYETHYLENE-BASED PASSIVE DIFFUSION BAG SAMPLERS TO OBTAIN VOLATILE ORGANIC COMPOUND CONCENTRATIONS IN WELLS

PART 1: DEPLOYMENT, RECOVERY, DATA INTERPETATION, AND QUALITY CONTROL AND ASSURANCE

Water-Resources Investigations Report 01-4060

Prepared in cooperation with the

U.S. AIR FORCE

U.S. NAVAL FACILITIES ENGINEERING COMMAND

U.S. ENVIRONMENTAL PROTECTION AGENCY

FEDERAL REMEDIATION TECHNOLOGIES ROUNDTABLE

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User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells

Part 1: Deployment, Recovery, Data Interpretation, and Quality Control and Assurance

By Don A. Vroblesky

U.S. Geological Survey

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Conversion Factors, Vertical Datum, Acronyms, and Abbreviations

Multiply	By	To obtain
<i>Length</i>		
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
<i>Area</i>		
square mile (mi ²)	2.590	square kilometer
<i>Flow</i>		
foot per day (ft/d)	0.3048	meter per day
foot squared per day (ft ² /d)	0.09294	meter squared per day
gallon per minute (gal/min)	0.06308	liter per second
gallon per day (gal/d)	0.003785	cubic meter per day
inch per year (in/yr)	25.4	millimeter per year
<i>Volume</i>		
gallon (gal)	3.785	liter

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation: °F = 9/5 (°C) + 32

Sea level refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Chemical concentration in water is expressed in metric units as milligrams per liter (mg/L) or micrograms per liter (µg/L).

Additional Abbreviations	
EDB	1,2-Dibromomethane
AFCEE	Air Force Center for Environmental Excellence
cDCE	cis-1,2-Dibromoethene
ft ³ /d	cubic feet per day
ft ³ /mg	cubic feet per milligram
°C	degrees Celsius
g	gram
ITRC	Interstate Technology Regulatory Cooperation
LDPE	low-density polyethylene
L	liter
µg	microgram
µm	micrometer
µL	microliter
mg	milligram
mL	milliliter
mL/min	milliliter per minute
MTBE	Methyl- <i>tert</i> -butyl ether
NAVFAC	Naval Facilities Engineering Command
NAPL	non-aqueous phase liquid
PDB	passive diffusion bag
PCE	Tetrachloroethene
TCE	Trichloroethene
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOA	Volatile organic analysis
VOC	Volatile organic compound

User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells

Part 1: Deployment, Recovery, Data Interpretation, and Quality Control and Assurance

By Don A. Vroblesky

EXECUTIVE SUMMARY

Water-filled passive diffusion bag (PDB) samplers described in this report are suitable for obtaining concentrations of a variety of volatile organic compounds (VOCs) in ground water at monitoring wells. The suggested application of the method is for long-term monitoring of VOCs in ground-water wells at well-characterized sites.

The effectiveness of the use of a single PDB sampler in a well is dependent on the assumption that there is horizontal flow through the well screen and that the quality of the water is representative of the ground water in the aquifer directly adjacent to the screen. If there are vertical components of intra-bore-hole flow, multiple intervals of the formation contributing to flow, or varying concentrations of VOCs vertically within the screened or open interval, then a multiple deployment of PDB samplers within a well may be more appropriate for sampling the well.

A typical PDB sampler consists of a low-density polyethylene (LDPE) lay-flat tube closed at both ends and containing deionized water. The sampler is positioned at the target horizon of the well by attachment to a weighted line or fixed pipe.

The amount of time that the sampler should be left in the well prior to recovery depends on the time required by the PDB sampler to equilibrate with ambient water and the time required for the environmental disturbance caused by sampler deployment to return to ambient conditions. The rate that the water within the PDB sampler equilibrates with ambient water depends on multiple factors, including the type of compound being sampled and the water temperature. The concentrations of benzene, *cis*-1,2-dichloroethene,

tetrachloroethene, trichloroethene, toluene, naphthalene, 1,2-dibromoethane, and total xylenes within the PDB samplers equilibrated with the concentrations in an aqueous mixture of those compounds surrounding the samplers under laboratory conditions within approximately 48 hours at 21 degrees Celsius (°C). A subsequent laboratory study of mixed VOCs at 10 °C showed that tetrachloroethene and trichloroethene were equilibrated by about 52 hours, but other compounds required longer equilibration times. Chloroethane, *cis*-1,2-dichloroethene, *trans*-1,2-dichloroethene, and 1,1-dichloroethene were not equilibrated at 52 hours, but appeared to be equilibrated by the next sampling point at 93 hours. Vinyl chloride, 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,1-dichloroethane were not equilibrated at 93 hours, but were equilibrated by the next sampling point at 166 hours. Different equilibration times may exist for other compounds. Differences in equilibration times, if any, between single-solute or mixed VOC solutions have not yet been thoroughly examined.

The samplers should be left in place long enough for the well water, contaminant distribution, and flow dynamics to restabilize following sampler deployment. Laboratory and field data suggest that 2 weeks of equilibration probably is adequate for many applications; therefore, a minimum equilibration time of 2 weeks is suggested. In less permeable formations, longer equilibration times may be required. When applying PDB samplers in waters colder than previously tested (10 °C) or for compounds without sufficient corroborating data, a side-by-side comparison with conventional methodology is advisable to justify the field equilibration time.

Following the initial equilibration period, the samplers maintain equilibrium concentrations with the ambient water until recovery. Thus, there is no specified time for sampler recovery after initial equilibration. PDB samplers routinely have been left in ground waters having concentrations of greater than 500 parts per million (ppm) of trichloroethene for 3 months at a time with no loss of bag integrity, and at one site, the PDB samplers have been left in place in VOC-contaminated ground water for 1 year with no reported loss of sampler integrity. The effects of long-term (greater than 1 month) PDB-sampler deployment on sampler and sample integrity have not yet been thoroughly tested for a broad range of compounds and concentrations, however. Moreover, in some environments, development of a biofilm on the polyethylene may be a consequence of long-term deployment. Investigations of semipermeable membrane devices (SPMDs) have shown that the transfer of some compounds across a heavily biofouled polyethylene membrane may be reduced, but not stopped. If a heavy organic coating is observed on a PDB sampler, it is advisable to determine the integrity of the sample by comparison to a conventional sampling method before continuing to use PDB samplers for long-term deployment in that well.

Recovery consists of removing the samplers from the well and immediately transferring the enclosed water to 40-milliliter sampling vials for analysis. The resulting concentrations represent an integration of chemical changes over the most recent portion of the equilibration period (approximately 48 to 166 hours, depending on the water temperature and the type of compound).

The method has both advantages and limitations when compared to other sampling methods. Advantages include the potential for PDB samplers to eliminate or substantially reduce the amount of purge water associated with sampling. The samplers are relatively inexpensive and easy to deploy and recover. Because PDB samplers are disposable, there is no downhole equipment to be decontaminated between wells, and there is a minimum amount of field equipment required. The samplers also have the potential to delineate contaminant stratification in the formation across the open or screened intervals of monitoring wells where vertical hydraulic gradients are not present. In addition, the samplers integrate concentrations over time, which may range between about 48 to 166 hours depending on the compound of interest. Because the pore size of LDPE is only about

10 angstroms or less, sediment does not pass through the membrane into the bag. Thus, PDB samplers are not subject to interferences from turbidity. In addition, none of the data collected suggest that VOCs leach from the LDPE material, or that there is a detrimental effect on the VOC sample from the PDB material.

Water-filled polyethylene PDB samplers are not appropriate for all compounds. The samplers are not suitable for inorganic ions and have a limited applicability for non-VOCs and for some VOCs. For example, although methyl-*tert*-butyl ether and acetone and most semivolatile compounds are transmitted through the polyethylene bag, laboratory tests have shown that the resulting concentrations were lower than in ambient water. A variety of factors influence the ability of compounds to diffuse through the polyethylene. These factors include the molecular size and shape and the hydrophobic nature of the compound. Unpublished laboratory test data of semivolatile compounds in contact with PDB samplers showed a higher concentration of phthalates inside the PDB sampler than outside the PDB sampler, suggesting that the polyethylene may contribute phthalates to the enclosed water. Thus, the samplers should not be used to sample for phthalates.

VOC concentrations in PDB samplers represent concentrations in the vicinity of the sampler within the well screen or open interval. This may be a limitation for PDB samplers and some other types of sampling, such as low-flow sampling, if the ground-water contamination is above or below the screen or not in the sample intervals providing water movement to the PDB samplers. If there is a vertical hydraulic gradient in the well, then the concentrations in the sampler may represent the concentrations in the water flowing vertically past the sampler rather than in the formation directly adjacent to the sampler. Vertically spaced multiple PDB samplers may be needed in chemically stratified wells or where flow patterns through the screen change as a result of ground-water pumping or seasonal water-level fluctuations.

The purposes of this document are to present methods for PDB sampler deployment, and recovery; to discuss approaches to determine the applicability of passive diffusion samplers; and to discuss various factors influencing interpretation of the data. The intended audience for the methodology sections of this report is managers and field personnel involved in using PDB samplers. The discussion of passive diffusion sampler applicability and interpretation of the data is

suited for project managers, technical personnel, and the regulatory community. Part 2 of this report presents case studies of PDB sampler field applications.

INTRODUCTION

The use of PDB samplers for collecting ground-water samples from wells offers a cost-effective approach to long-term monitoring of VOCs at well-characterized sites (Vroblesky and Hyde, 1997; Gefell and others, 1999). The effectiveness of the use of a single PDB sampler in a well is dependent on the assumption that there is horizontal flow through the well screen and that the quality of the water is representative of the ground water in the aquifer directly adjacent to the screen. If there are vertical components of intra-borehole flow, multiple intervals of the formation contributing to flow, or varying concentrations of VOCs vertically within the screened or open interval, then deployment of multiple PDB samplers within a well may be more appropriate for sampling the well.

The samplers consist of deionized water enclosed in a LDPE sleeve (fig. 1) and are deployed adjacent to a target horizon within a screened or open interval of a well. The suggested application is for long-term monitoring of VOCs in ground-water wells. Where the screened interval is greater than 10 feet (ft), the potential for contaminant stratification and/or intra-borehole flow within the screened interval is greater than in screened intervals shorter than 10 ft. It is important that the vertical distribution of contaminants be determined in wells having 10-ft-long well screens, and that both the vertical distribution of contaminants and the potential for intra-borehole flow be determined in wells having screens longer than 10 ft. For many VOCs of environmental interest (table 1), the VOC concentration in water within the sampler approaches the VOC concentration in water outside of the PDB sampler over an equilibration period. The resulting concentrations represent an integration of chemical changes over the most recent part of the equilibration period (approximately 48 to 166 hours, depending on the water temperature and the type of compound being sampled). The approach is inexpensive and has the potential to eliminate or substantially reduce the amount of purge water removed from the well.

A variety of PDB samplers have been utilized in well applications (fig. 1). Although the samplers vary in specific construction details, a typical PDB sampler consists of a 1- to 2-ft-long LDPE tube closed at both ends and containing laboratory-grade deionized water (fig. 1). The typical diameter for PDB samplers used in a 2-inch-diameter well is approximately 1.2 inches; however, other dimensions may be used to match the well diameter. Equilibration times may be longer for larger diameter PDB samplers. On the outside of the PDB sampler, a low-density polyethylene-mesh sometimes is used for protection against abrasion in open boreholes and as a means of attachment at the prescribed depth. The PDB sampler can be positioned at the target horizon by attachment to a weighted line or by attachment to a fixed pipe.

PDB samplers for use in wells are available commercially. Authorized distributors as of March 2001 are Columbia Analytical Services (800-695-7222) and Eon Products (800-474-2490). A current list of vendors and PDB-sampler construction details can be obtained from the U.S. Geological Survey Technology Transfer Enterprise Office, Mail Stop 211, National Center, 12201 Sunrise Valley Drive, Reston, Virginia 20192 (telephone 703-648-4344; fax 703-648-4408). PDB samplers employ patented technology (U.S. patent number 5,804,743), and therefore, require that the user purchase commercially produced samplers from a licensed manufacturer or purchase a nonexclusive license for sampler construction from the U.S. Geological Survey Technology Enterprise Office at the above address.

The purposes of this document are to present methods for PDB sampler deployment, and recovery; to discuss approaches for determining the applicability of passive diffusion samplers; and to discuss various factors influencing interpretation of the data. The intended audience for the methodology sections of this report is managers and field personnel involved in using PDB samplers. The discussion of PDB sampler applicability and interpretation of the data is suited for project managers, technical personnel, and the regulatory community. Part 2 of this report presents case studies of PDB-sampler field applications.



Figure 1. Typical water-filled passive diffusion bag samplers used in wells, including (A) diffusion bag with polyethylene mesh, (B) diffusion bag without mesh, and (C) bag and mesh attached to bailer bottom.

Table 1. Compounds tested under laboratory conditions for use with passive diffusion bag samplers [From Vroblesky and Campbell, 2001]

Tested compounds showing good correlation (average differences in concentration of 11 percent or less between diffusion-sampler water and test-vessel water) in laboratory tests			
Benzene	2 Chlorovinyl ether	<i>cis</i> -1,2-Dichloroethene	1,1,1-Trichloroethane
Bromodichloromethane	Dibromochloromethane	<i>trans</i> -1,2-Dichloroethene	1,1,2-Trichloroethane
Bromoform	Dibromomethane	1,2-Dichloropropane	Trichloroethene
Chlorobenzene	1,2-Dichlorobenzene	<i>cis</i> -Dichloropropene	Trichlorofluoromethane
Carbon tetrachloride	1,3-Dichlorobenzene	1,2-Dibromoethane	1,2,3-Trichloropropane
Chloroethane	1,4-Dichlorobenzene	<i>trans</i> -1,3-Dichloropropene	1,1,2,2-Tetrachloroethane
Chloroform	Dichlorodifluoromethane	Ethyl benzene	Tetrachloroethene
Chloromethane	1,2-Dichloroethane	Naphthalene	Vinyl chloride
	1,1-Dichloroethene	Toluene	Total xylenes
Tested compounds showing poor correlation (average differences in concentration greater than 20 percent between diffusion-sampler water and test-vessel water) in laboratory tests			
Acetone*	Methyl- <i>tert</i> -butyl ether	Styrene	

*T.M Sivavec and S.S. Baghel, General Electric Company, written commun., 2000

Summary of Passive Diffusion Bag Sampler Advantages and Limitations

Advantages

1. PDB samplers have the potential to eliminate or substantially reduce the amount of purge water associated with sampling.

2. PDB samplers are inexpensive.

3. The samplers are easy to deploy and recover.

4. Because PDB samplers are disposable, there is no downhole equipment to be decontaminated between wells.

5. A minimal amount of field equipment is required.

6. Sampler recovery is rapid. Because of the small amount of time and equipment required for the sampling event, the method is practical for use where access is a problem or where discretion is desirable (that is, residential communities, business districts, or busy streets where vehicle traffic control is a concern).

7. Multiple PDB samplers, distributed vertically along the screened or open interval, may be used in conjunction with borehole flow meter testing to gain insight on the movement of contaminants into and out of the well screen or open interval or to locate the zone of highest concentration in the well. Analytical costs when using multiple PDB samplers sometimes can be reduced by selecting a limited number of the samplers for laboratory analysis based on screening by using field gas chromatography at the time of sample collection.

8. Because the pore size of LDPE is only about 10 angstroms or less, sediment does not pass through the membrane into the bag. Thus, PDB samplers are not subject to interferences from turbidity. In addition, none of the data collected suggest that VOCs leach from the LDPE material or that there is a detrimental effect from the PDB material on the VOC sample.

Limitations

1. PDB samplers integrate concentrations over time. This may be a limitation if the goal of sampling is to collect a representative sample at a point in time in an aquifer where VOC-concentrations substantially change more rapidly than the samplers equilibrate. Laboratory results obtained indicate that a variety of compounds equilibrated within 48 hours at 21 °C (Vroblesky and Campbell, 2001). Vinyl chloride, 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,1-dichloroethane may require between 93 and 166 hours to equilibrate at 10 °C (T.M. Sivavec and S.S. Baghel, General Electric Company, written commun., 2000). The initial equilibration under field conditions may be longer to allow

well water, contaminant distribution, and flow dynamics to restabilize following sampler deployment.

2. Water-filled polyethylene PDB samplers are not appropriate for all compounds. For example, although methyl-*tert*-butyl ether and acetone (Vroblesky, 2000; Paul Hare, General Electric Company, oral commun., 2000) and most semivolatile compounds are transmitted through the polyethylene bag, laboratory tests have shown that the resulting concentrations were lower than in ambient water. A variety of factors influence the ability of compounds to diffuse through the polyethylene membrane. These factors include the molecular size and shape and the hydrophobic nature of the compound. Compounds having a cross-sectional diameter of about 10 angstroms or larger (such as humic acids) do not pass through the polyethylene because the largest (transient) pores in polyethylene do not exceed about 10 angstroms in diameter (Flynn and Yalkowsky, 1972; Hwang and Kammermeyer, 1975; Comyn, 1985). The samplers are not appropriate for hydrophilic polar molecules, such as inorganic ions. A detailed discussion of the relation between hydrophobicity and compound transport through polyethylene can be found in Gale (1998). Unpublished laboratory test data (D.A. Vroblesky, U.S. Geological Survey, written commun., 1998) of semi-volatile compounds in contact with PDB samplers showed a higher concentration of phthalates inside the PDB sampler than outside the PDB sampler, suggesting that the polyethylene may contribute phthalates to the enclosed water. Thus, the samplers should not be used to sample for phthalates.

3. PDB samplers rely on the free movement of water through the well screen. In situations where ground water flows horizontally through the well screen, the VOC concentrations in the open interval of the well probably are representative of the aquifer water in the adjacent formation (Gillham and others, 1985; Robin and Gillham, 1987; Kearn and others, 1992; Powell and Puls, 1993; Vroblesky and Hyde, 1997). In these situations, the VOC concentration of the water in contact with the PDB samplers, and therefore, the water within the diffusion samplers, probably represents local conditions in the adjacent aquifer. However, if the well screen is less permeable than the aquifer or the sandpack, then under ambient conditions, flowlines may be diverted around the screen. Such a situation may arise from inadequate well development or from iron bacterial fouling of the well screen. In this case, the VOC concentrations in the PDB samplers may not represent concentrations in

the formation water because of inadequate exchange across the well screen. PDB samplers have not yet been adequately tested to determine their response under such conditions.

4. VOC concentrations in PDB samplers represent ground-water concentrations in the vicinity of the screened or open well interval that move to the sampler under ambient flow conditions. This is a limitation if the ground-water contamination lies above or below the well screen or open interval, and requires the operation of a pump to conduct contaminants into the well for sampling.

5. In cases where the well screen or open interval transects zones of differing hydraulic head and variable contaminant concentrations, VOC concentrations obtained using a PDB sampler may not reflect the concentrations in the aquifer directly adjacent to the sampler because of vertical transport in the well. However, a vertical array of PDB samplers, used in conjunction with borehole flow meter testing, can provide insight on the movement of contaminants into or out of the well. This information then can be used to help determine if the use of PDB samplers is appropriate for the well, and to select the optimal vertical location(s) for the sampler deployment.

6. In wells with screens or open intervals with stratified chemical concentrations, the use of a single PDB sampler set at an arbitrary (by convention) depth may not provide accurate concentration values for the most contaminated zone. However, multiple PDB samplers distributed vertically along the screened or open interval, in conjunction with pump sampling (as appropriate), can be used to locate zone(s) of highest concentration in the well. Multiple PDB samplers also may be needed to track the zone of maximum concentration in wells where flow patterns through the screened interval change as a result of ground-water pumping or seasonal water-table fluctuations.

PASSIVE DIFFUSION BAG SAMPLER DEPLOYMENT

A variety of approaches can be used to deploy the PDB samplers in wells. A typical deployment approach, described in this section, is to attach the PDB samplers to a weighted line. It also is acceptable to attach the weights directly to the PDB sampler if the attachment point is of sufficient strength to support the weight. The weights attached to the bottom of the

line are stainless steel and can be reused, but must be thoroughly decontaminated with a detergent before the first use or before using in a different well. Rope, such as 90 pound, 3/16 inch braided polyester, can be used as the line for single-use applications if it is of sufficient strength to support the weight and sampler, is nonbuoyant, and is subject to minimal stretch; however, the rope should not be reused because of the high potential for cross contamination. Stainless-steel or Teflon-coated stainless-steel wire is preferable. The weighted lines should not be reused in different wells to prevent carryover of contaminants. A possible exception is coated stainless-steel wire, which can be reused after sufficient decontamination. An alternative deployment approach, not discussed in this section, is to attach the PDB samplers to a fixed pipe in the well (Vroblesky and Peters, 2000, p. 3; also included in Part 2 of this publication). The PDB samplers should not contact non-aqueous phase liquid (NAPL) during deployment or retrieval to prevent cross contamination. An approach that can be utilized to deploy diffusion samplers through a layer of floating NAPL is described in the field test at Naval Station North Island, California (Vroblesky and Peters, 2000, p. 3-4; also included in Part 2 of this publication).

If the PDB sampler is to be compared with a conventional pumping approach to sampling, then it is suggested that both the pump and the PDB sampler be deployed at the same time, with the sampler attached near (such as directly below) the pump inlet. This approach eliminates potential concentration differences between the two methods that may result from well disturbance during equipment removal and deployment at the time of sampling. An alternative method is to deploy the PDB samplers independently of the pumps and recover the samplers immediately prior to placing the pump down the well.

PDB samplers are available either prefilled with laboratory-grade deionized water or unfilled. The unfilled samplers are equipped with a plug and funnel to allow for field filling and sample recovery. To fill these samplers, remove the plug from the sampler bottom, insert the short funnel into the sampler, and pour laboratory-grade deionized water into the sampler. The sampler should be filled until water rises and stands at least half way into the funnel. Remove excess bubbles from the sampler. Remove the funnel and reattach the plug. A small air bubble from the plug is of no concern.

The following steps should be used for deploying PDB samplers in wells:

1. Measure the well depth and compare the measured depth with the reported depth to the bottom of the well screen from well-construction records. This is to check on whether sediment has accumulated in the bottom of the well, whether there is a nonscreened section of pipe (sediment sump) below the well screen, and on the accuracy of well-construction records. If there is an uncertainty regarding length or placement of the well screen, then an independent method, such as video imaging of the well bore, is strongly suggested.

2. Attach a stainless-steel weight to the end of the line. Sufficient weight should be added to counterbalance the buoyancy of the PDB samplers. This is particularly important when multiple PDB samplers are deployed. One approach, discussed in the following paragraphs, is to have the weight resting on the bottom of the well, with the line taut above the weight. Alternatively, the PDB sampler and weight may be suspended above the bottom, but caution should be exercised to ensure that the sampler does not shift location. Such shifting can result from stretching or slipping of the line or, if multiple samplers are attached end-to-end rather than to a weighted line, stretching of the samplers.

3. Calculate the distance from the bottom of the well, or top of the sediment in the well, up to the point where the PDB sampler is to be placed. A variety of approaches can be used to attach the PDB sampler to the weight or weighted line at the target horizon. The field-fillable type of PDB sampler is equipped with a hanger assembly and weight that can be slid over the sampler body until it rests securely near the bottom of the sampler. When this approach is used with multiple PDB samplers down the same borehole, the weight should only be attached to the lowermost sampler. An additional option is to use coated stainless-steel wire as a weighted line, making loops at appropriate points to attach the upper and lower ends of PDB samplers. Where the PDB sampler position varies between sampling events, movable clamps with rings can be used. When using rope as a weighted line, a simple approach is to tie knots or attach clasps at the appropriate depths. Nylon cable ties or stainless-steel clips inserted through the knots can be used to attach the PDB samplers. An approach using rope as a weighted line with knots tied at the appropriate sampler-attachment points is discussed below.

- (a) For 5-ft-long or shorter well screens, the center point of the PDB sampler should be the vertical midpoint of the saturated well-screen length. For example, if the well screen is at a depth of 55 to 60 ft below the top of casing, and the measured depth of the well is 59 ft, then the bottom of the well probably has filled with sediment. In this case, the midpoint of the sampler between the attachment points on the line will be midway between 55 and 59 ft, or at 57 ft. Thus, for a 1.5-ft-long sampler, the attachment points on a weighted line should be tied at distances of 1.25 ft ($2 \text{ ft} - 0.75 \text{ ft}$) and 2.75 ft ($2 \text{ ft} + 0.75 \text{ ft}$) from the top of the sediment in the well, or the bottom of the well, making adjustments for the length of the attached weight. When the PDB sampler is attached to the line and installed in the well, the center of the sampler will be at 57-ft depth. If, however, independent evidence is available showing that the highest concentration of contaminants enters the well from a specific zone within the screened interval, then the PDB sampler should be positioned at that interval.

- (b) For 5- to 10-ft-long well screens, it is advisable to utilize multiple PDB samplers vertically along the length of the well screen for at least the initial sampling (fig. 2). The purposes of the multiple PDB samplers are to determine whether contaminant stratification is present and to locate the zone of highest concentration. The midpoint of each sampler should be positioned at the midpoint of the interval to be sampled. For 1.5-ft-long samplers, at each sampling depth in the screened interval, make two attachment points on the weighted line at a distance of about 1.5 ft apart. The attachment points should be positioned along the weighted line at a distance from the bottom end of the weight such that the midpoint between the knots will be at the desired sampling depth along the well screen. Sampler intervals are variable, but a simple approach is to use the top knot/loop of one sampler interval as the bottom knot/loop for the overlying sampler interval.



Figure 2. Example of multiple PDB samplers prepared for deployment.

(c) PDB samplers should not be used in wells having screened or open intervals longer than 10 ft unless used in conjunction with borehole flow meters or other techniques to characterize vertical variability in hydraulic conductivity and contaminant distribution or used strictly for qualitative reconnaissance purposes. This is because of the increased potential for cross contamination of water-bearing zones and hydraulically driven mixing effects that may cause the contaminant stratification in the well to differ from the contaminant stratification in the adjacent aquifer material. If it is necessary to sample such wells, then multiple PDB samplers should be installed vertically across the screened or open interval to determine the zone of highest concentration and whether contaminant stratification is present.

4. The samplers should be attached to the weights or weighted line at the time of deployment. For samplers utilizing the hanger and weight assembly,

the line can be attached directly to the top of the sampler. PDB samplers utilizing an outer protective mesh can be attached to a weighted line by using the following procedure:

(a) Insert cable ties through the attachment points in the weighted line.

(b) At each end of the PDB sampler, weave the ends of the cable ties or clamp through the LPDE mesh surrounding the sampler and tighten the cable ties. Thus, each end of the PDB sampler will be attached to a knot/loop in the weighted line by means of a cable tie or clamp. The cable ties or clamps should be positioned through the polyethylene mesh in a way that prevents the PDB sampler from sliding out of the mesh.

(c) Trim the excess from the cable tie before placing the sampler down the well. Caution should be exercised to prevent sharp edges on the trimmed cable ties that may puncture the LDPE.

5. When using PDB samplers without the protective outer mesh, the holes punched at the ends of the bag, outside the sealed portion, can be used to attach the samplers to the weighted line. Stainless-steel spring clips have been found to be more reliable than cable ties in this instance, but cable ties also work well.

6. Lower the weight and weighted line down the well until the weight rests on the bottom of the well and the line above the weight is taut. The PDB samplers should now be positioned at the expected depth. A check on the depth can be done by placing a knot or mark on the line at the correct distance from the top knot/loop of the PDB sampler to the top of the well casing and checking to make sure that the mark aligns with the lip of the casing after deployment.

7. Secure the assembly in this position. A suggested method is to attach the weighted line to a hook on the inside of the well cap. Reattach the well cap. The well should be sealed in such a way as to prevent surface-water invasion. This is particularly important in flush-mounted well vaults that are prone to flooding.

8. Allow the system to remain undisturbed as the PDB samplers equilibrate.

PASSIVE DIFFUSION BAG SAMPLER AND SAMPLE RECOVERY

The amount of time that the samplers should be left in the well prior to recovery depends on the time required by the PDB sampler to equilibrate with ambient water and the time required for environmental disturbances caused by sampler deployment to return to ambient conditions. The rate that the water within the PDB sampler equilibrates with ambient water depends on multiple factors, including the type of compound being sampled and the water temperature. The concentrations of benzene, *cis*-1,2-dichloroethene (cDCE), tetrachlorethene (PCE), trichloroethene (TCE), toluene, naphthalene, 1,2-dibromoethane (EDB), and total xylenes within the PDB samplers equilibrated with the concentrations in an aqueous mixture of those compounds surrounding the samplers under laboratory conditions within approximately 48 hours at 21 °C (Vroblesky and Campbell, 2001). A subsequent laboratory study of mixed VOCs at 10 °C showed that PCE and TCE were equilibrated by about 52 hours, but other compounds required longer equilibration times (T.M. Sivavec and S.S. Baghel, General Electric Company, written commun., 2000). Chloroethane, cDCE, *trans*-1,2-dichloroethene, and 1,1-dichloroethene were not

equilibrated at 52 hours, but appeared to be equilibrated by the next sampling point at 93 hours. Vinyl chloride, 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,1-dichloroethane were not equilibrated at 93 hours, but were equilibrated by the next sampling point at 166 hours. Different equilibration times may exist for other compounds. Differences in equilibration times, if any, between single-solute or mixed-VOC solutions have not yet been thoroughly examined.

Under field conditions, the samplers should be left in place long enough for the well water, contaminant distribution, and flow dynamics to restabilize following sampler deployment. The results of borehole dilution studies show that wells can recover to 90 percent of the predisturbance conditions within minutes to several hours for permeable to highly permeable geologic formations, but may require 100 to 1,000 hours (4 to 40 days) in muds, very fine-grained loamy sands, and fractured rock, and may take even longer in fractured shales, recent loams, clays, and slightly fractured solid igneous rocks (Halevy and others, 1967).

In general, where the rate of ground-water movement past a diffusion sampler is high, equilibration times through various membranes commonly range from a few hours to a few days (Mayer, 1976; Harrington and others, 2000). One field investigation showed adequate equilibration of PDB samplers to aquifer trichloroethene (TCE) and carbon tetrachloride (CT) concentrations within 2 days in a highly permeable aquifer (Vroblesky and others, 1999). In other investigations, PDB samplers recovered after 14 days were found to be adequately equilibrated to chlorinated VOCs (Obrien & Gere Engineers, Inc., 1997a, 1997b; Hare, 2000); therefore, the equilibration period was less than or equal to 14 days for those field conditions. Because it appears that 2 weeks of equilibration probably is adequate for many applications, a minimum equilibration time of 2 weeks is suggested. When applying PDB samplers in waters colder than previously tested (10 °C) or for compounds without sufficient corroborating field data, a side-by-side comparison with conventional sampling methodology is advisable to justify the field equilibration time.

In less permeable formations, longer equilibration times may be required. It is probable that water in the well bore eventually will equilibrate with the pore-water chemistry; however, if the rate of chemical change or volatilization loss in the well bore exceeds the rate of exchange between the pore water and the well-bore water, then the PDB samplers may under-

estimate pore-water concentrations. Guidelines for equilibration times and applicability of PDB samplers in low-permeability formations have not yet been established. Therefore, in such situations, a side-by-side comparison of PDB samplers and conventional sampling methodology is advisable to ensure that the PDB samplers do not underestimate concentrations obtained by the conventional method. A detailed discussion of diffusion rates relevant to diffusion sampler equilibrium in slow-moving ground-water systems can be found in Harrington and others (2000).

Following the initial equilibration period, the samplers maintain equilibrium concentrations with the ambient water until recovery. Thus, there is no specified maximum time for sampler recovery. PDB samplers have routinely been left in ground waters having concentrations of greater than 500 ppm of TCE for 3 months at a time with no loss of bag integrity, and at one site, the PDB samplers have been left in place in VOC-contaminated ground water for 1 year with no reported loss of sampler integrity (Paul Hare, General Electric Company, oral commun., 2000). The effects of long-term (greater than 1 month) PDB-sampler deployment on sampler and sample integrity have not yet been thoroughly tested for a broad range of compounds and concentrations. Moreover, in some environments, development of a biofilm on the polyethylene may be a consequence of long-term deployment. Investigations of semipermeable membrane devices (SPMDs) have shown that the transfer of some compounds may be reduced, but not stopped, across a heavily biofouled polyethylene membrane (Ellis and others, 1995; Huckins and others, 1996; Huckins and others, in press). If a heavy organic coating is observed on a PDB sampler, it is advisable to determine the integrity of the sample by comparing contaminant concentrations from the PDB sampler to concentrations from a conventional sampling method before continuing to use PDB samplers for long-term deployment in that well.

Recovery of PDB samplers is accomplished by using the following approach:

1. Remove the PDB samplers from the well by using the attached line. The PDB samplers should not be exposed to heat or agitated.

2. Examine the surface of the PDB sampler for evidence of algae, iron or other coatings, and for tears in the membrane. Note the observations in a sampling field book. If there are tears in the membrane, the

sample should be rejected. If there is evidence that the PDB sampler exhibits a coating, then this should be noted the validated concentration data.

3. Detach and remove the PDB sampler from the weighted line. Remove the excess liquid from the exterior of the bag to minimize the potential for cross contamination.

4. A variety of approaches may be used to transfer the water from the PDB samplers to 40-mL volatile organic analysis (VOA) vials. One type of commercially available PDB sampler provides a discharge device that can be inserted into the sampler. If discharge devices are used, the diameter of the opening should be kept to less than about 0.15 inches to reduce volatilization loss. Two options are presently available to recover water from the sample using discharge devices. One option involves removing the hanger and weight assembly from the sampler, inverting the sampler so that the fill plug is pointed upward, and removing the plug. The water can be recovered by directly pouring in a manner that minimizes agitation or by pouring through a VOC-discharge accessory inserted in place of the plug. The second approach involves piercing the sampler near the bottom with a small-diameter discharge tube and allowing water to flow through the tube into the VOA vials. In each case, flow rates can be controlled by tilting or manipulating the sampler. Alternatively, the PDB sampler can be cut open at one end using scissors or other cutting devices which have been decontaminated between use for different wells. Water can then be transferred to 40-ml VOA vials by gently pouring in a manner that minimizes water agitation. Acceptable duplication has been obtained using each method. Preserve the samples according to the analytical method. The sampling vials should be stored at approximately 4 °C in accordance with standard sampling protocol. Laboratory testing suggests that there is no substantial change in the VOC concentrations in PDB samplers over the first several minutes after recovery; however, the water should be transferred from the water-filled samplers to the sample bottles immediately upon recovery.

5. A cost-effective alternative when using multiple PDB samplers in a single well is to field screen water from each sampler using gas chromatography. These results can be used to decide which of the multiple PDB samplers should be sent to an EPA-approved laboratory for standard analysis. Typically, at least the sample containing the highest concentration should be analyzed by a laboratory.

6. If a comparison is being made between concentrations obtained using PDB samplers and concentrations obtained using a conventional sampling approach, then the well should be sampled by the conventional approach soon after (preferably on the same day) recovery of the PDB sampler. The water samples obtained using PDB samplers should be sent in the same shipment, as the samples collected by the conventional approach for the respective wells. Utilizing the same laboratory may reduce analytical variability.

7. Any unused water from the PDB sampler and water used to decontaminate cutting devices should be disposed in accordance with local, state, and Federal regulations.

DETERMINING APPLICABILITY OF PASSIVE DIFFUSION BAG SAMPLERS AND INTERPRETATION OF DATA

When attempting to determine whether the use of PDB samplers is appropriate at a particular well, a common approach is to do a side-by-side comparison with a conventional sampling method during the same sampling event. This approach is strongly suggested in wells having temporal concentration variability. In a well having relatively low temporal concentration variability, comparison of the PDB-sampler results to historical concentrations may provide enough information to determine whether the PDB samplers are appropriate for the well. In general, if both PDB and conventional sampling produce concentrations that agree within a range deemed acceptable by local, state, and Federal regulatory agencies and meet the site-specific data-quality objectives, then a PDB sampler may be approved for use in that well to monitor ambient VOC concentrations. If concentrations from the PDB sampler are higher than concentrations from the conventional method, it is probable that concentrations from the PDB sampler adequately represent ambient conditions because there usually is a greater potential for dilution from mixing during sampling using conventional methods than during sampling using PDB samplers.

If, however, the conventional method produces concentrations that are significantly higher than those obtained using the PDB sampler, then it is uncertain whether the PDB-sampler concentrations represent local ambient conditions. In this case, further testing can be done to determine whether contaminant stratification and/or intra-borehole flow is present. Multiple sampling devices can be used to determine the pres-

ence of contaminant stratification, and borehole flow-meters can be used to determine whether intra-borehole flow is present. When using flowmeters to measure vertical flow in screened boreholes, however, the data should be considered qualitative because of the potential for water movement through the sand pack. Borehole dilution tests (Halevy and others, 1967; Drost and others, 1968; Grisak and others, 1977; Palmer, 1993) can be used to determine whether water is freely exchanged between the aquifer and the well screen.

Once the source of the difference between the two methods is determined, a decision can be made regarding the well-specific utility of the PDB samplers. Tests may show that VOC concentrations from the PDB samplers adequately represent local ambient conditions within the screened interval despite the higher VOC concentration obtained from the conventional method. This may be because the pumped samples incorporated water containing higher concentrations either from other water-bearing zones induced along inadequate well seals or through fractured clay (Vroblesky and others, 2000), from other water-bearing zones not directly adjacent to the well screen as a result of well purging prior to sampling (Vroblesky and Petkewich; 2000), or from mixing of chemically stratified zones in the vicinity of the screened interval (Vroblesky and Peters, 2000).

The mixing of waters from chemically stratified zones adjacent to the screened interval during pumping probably is one of the more important sources of apparent differences between the results obtained from PDB sampling and conventional sampling because such stratification probably is common. Vertical stratification of VOCs over distances of a few feet has been observed in aquifer sediments by using multilevel sampling devices (Dean and others, 1999; Pitkin and others, 1999), and considerable variation in hydraulic conductivity and water chemistry has been observed in an aquifer in Cape Cod, Massachusetts, on the scale of centimeters (Wolf and others, 1991; Smith and others 1991; Hess and others, 1992). Multiple PDB samplers have been used to show a change in TCE concentration of 1,130 ($\mu\text{g/L}$) over a 6-ft vertical screened interval in Minnesota (Vroblesky and Petkewich, 2000). Tests using PDB samplers in screened intervals containing VOC stratification showed that the PDB-sampler data appeared to be point-specific, whereas the pumped sample integrated water over a larger interval (Vroblesky and Peters, 2000).

The decision on whether to use PDB samplers in such situations depends on the data-quality objectives for the particular site. If the goal is to determine and monitor higher concentrations or to examine contaminant stratification within the screened interval, then the PDB samplers may meet this objective. If the goal is to determine the average concentrations for the entire screened interval, then a pumped sample or an average from multiple diffusion samplers may be appropriate.

As an aid in the decision-making process, the following section examines the influences that hydraulic and chemical heterogeneity of an aquifer can have on sample quality in long-screened wells. Because VOC concentrations from PDB samplers commonly are compared to VOC concentrations from other sampling methodologies, the second section examines the differences in sample quality between these methodologies in situations of hydraulic and chemical heterogeneity.

Influences of Hydraulic and Chemical Heterogeneity on Sample Quality in Long-Screened Wells

Sampling biases and chemical variability in long-screened wells, which can be loosely defined as wells having significant physical and chemical heterogeneity within the screened interval and in the adjacent aquifer (Reilly and LeBlanc, 1998), have been the subject of numerous investigations. Sources of chemical variability in such wells include non-uniform flow into wells (Robbins and Martin-Hayden, 1991; Reilly and Gibbs, 1993; Chiang and others, 1995; Church and Granato, 1996; Reilly and LeBlanc, 1998), lithologic heterogeneity (Reilly and others, 1989; Robbins, 1989; Martin-Hayden and others, 1991; Gibbs and others, 1993; Reilly and Gibbs, 1993), and in-well mixing. In a well open across a chemically or hydraulically heterogeneous section of the aquifer, differences in the sampling methodology can produce significant differences in the sampling results.

Long-screened wells have the potential to redistribute chemical constituents in the aquifer where there are vertical hydraulic gradients within the screened interval. Water can move into the well from one horizon and exit the well at a different horizon (Church and Granato, 1996; Reilly and LeBlanc 1998). If there is vertical flow in the screened or open interval, and the zone of low hydraulic head (outflow from

the well) is within the contaminated horizon, then the PDB samplers (or any standard sampling methodology) can underestimate or not detect the contamination. The reason is that, in this case, the contaminated horizon does not contribute water to the well under static conditions. Instead, water from other horizons with higher hydraulic head will invade the contaminated horizon by way of the well screen. Under pumped conditions, the majority of the extracted water will be from the most permeable interval, which may not be the contaminated zone. Even when pumping induces inflow from the contaminated interval, much of that inflow will be a reflection of the residual invaded water from other horizons. In this situation, a substantial amount of purging would be required before water representative of the aquifer could be obtained (Jones and Lerner, 1995). Such sampling is not likely to reflect a significant contribution from the contaminated zone, and concentrations in the contaminated zone probably will be underestimated.

Similarly, if VOC-contaminated water is flowing into the well and is exiting the well at a different horizon, then VOCs will be present along the screened interval between the two horizons. In this case, VOC concentrations in the screened interval may be representative of aquifer concentrations at the inflow horizon, but may not be representative of aquifer concentrations near the outflow horizon.

In areas where vertical stratification of VOC concentrations are anticipated, using multiple PDB samplers may more fully characterize the contaminated horizon than using a single PDB sampler. This is particularly true in wells having screens 10 ft or longer; however, significant VOC stratification has been observed over intervals of less than 5 ft (Vroblesky and Peters, 2000). Because of the increased probability of vertical concentration or hydraulic gradients within the open interval of long-screened (greater than 10 ft) wells, it is advisable to determine the zones of inflow and outflow within the screened or open interval of these wells using borehole flowmeter analysis (Hess, 1982; 1984; 1986; 1990; Young and others, 1998).

Comparison of Passive Diffusion Bag Sampling Methodology to Conventional Methodologies

Traditional sampling methodologies, such as the purge-and-sample (or conventional purging method), low-flow or low-volume sampling, and using straddle packers and multilevel samplers, produce VOC

concentrations that may differ from VOC concentrations obtained from PDB samplers because the methodologies sometimes are influenced in different ways by aquifer hydraulic and chemical heterogeneity. This section examines potential sources of concentration differences between traditional methodologies and the PDB methodology.

The purge-and-sample approach to ground-water monitoring differs from the diffusion-sampler approach primarily because the area of the screened or open interval that contributes water to the purged sample typically is greater than for the PDB sampler and the potential for mixing of stratified layers is higher. When pumping three or more casing volumes of water prior to collecting a sample, chemical concentrations in the discharging water typically change as the well is pumped (Keely and Boateng, 1987; Cohen and Rabold, 1988; Martin-Hayden and others, 1991; Robbins and Martin-Hayden, 1991; Reilly and Gibbs, 1993; Barcelona and others, 1994; Martin-Hayden, 2000), due to mixing during pumping and other factors, such as the removal of stagnant water in the casing and changing patterns of inflow and outflow under ambient and pumping conditions (Church and Granato, 1996). The induction of lateral chemical heterogeneity during pumping also may produce variations in the sampled concentrations. The amount of mixing during purging can be highly variable (Barber and Davis, 1987; Church and Granato, 1996; Reilly and LeBlanc, 1998; Martin-Hayden, 2000), and may result in concentrations that are not locally representative (Reilly and Gibbs, 1993). Substantial vertical hydraulic gradients, even in shallow homogeneous aquifers, have been observed to bias sampling using conventional purging because the majority of the pumped water may come from a particular horizon not related to the contaminated zone and because the intra-well flow that intruded the aquifer may not be adequately removed during purging (Hutchins and Acree, 2000). Thus, differences may be observed between concentrations obtained from a pumped sample and from a PDB sample in a chemically stratified interval if the pumped sample represents an integration of water collected from multiple horizons and the PDB sampler represents water collected from a single horizon.

Low-flow purging and sampling (Barcelona and others, 1994; Shanklin and others, 1995) disturbs the local ground water less than conventional purge-and-

sample methods. Thus, samples obtained by PDB samplers are likely to be more similar to samples obtained by using low-flow purging than to those obtained by using conventional purge-and-sample methods. Even under low-flow conditions, however, purging still can integrate water within the radius of pumping influence, potentially resulting in a deviation from VOC concentrations obtained by PDB sampling. One investigation found that in low hydraulic conductivity formations, low-flow sampling methodology caused excessive drawdown, which dewatered the screened interval, increased local ground-water velocities, and caused unwanted colloid and soil transport into the ground-water samples (Sevee and others, 2000). The authors suggest that in such cases, a more appropriate sampling methodology may be to collect a slug or passive sample from the well screen under the assumption that the water in the well screen is in equilibrium with the surrounding aquifer.

Isolating a particular contributing fracture zone with straddle packers in an uncased borehole allows depth-discrete samples to be collected from the target horizon (Hsieh and others, 1993; Kaminsky and Wylie, 1995). Strategically placed straddle packers often can minimize or eliminate the impact of vertical gradients in the sampled interval. However, even within a packed interval isolating inflowing fracture zones, deviations between VOC concentrations in water from PDB samplers and water sampled by conventional methods still may occur if the conventional method mixes chemically stratified water outside the borehole or if the packed interval straddles chemically heterogeneous zones.

The use of multilevel PDB samplers and other types of multilevel samplers (Ronen and others, 1987; Kaplan and others, 1991; Schirmer and others, 1995; Gefell and others, 1999; Jones and others, 1999) potentially can delineate some of the chemical stratification. Diffusion sampling and other sampling methodologies, however, can be influenced by vertical hydraulic gradients within the well screen or the sand pack. When vertical hydraulic gradients are present within the well, water contacting the PDB sampler may not be from a horizon adjacent to the PDB sampler. Rather, the water may represent a mixing of water from other contributing intervals within the borehole. In a screened well, even multilevel samplers with baffles to limit vertical flow in the well cannot prevent influences from

vertical flow in the gravel pack outside the well screen. Such vertical flow can result from small vertical differences in head with depth. A field test conducted by Church and Granato (1996) found that vertical head differences ranging from undetectable to 0.49 ft were sufficient to cause substantial flows (as much as 0.5 liters/minute) in the well bore.

QUALITY CONTROL AND ASSURANCE

The sources of variability and bias introduced during sample collection can affect the interpretation of the results. To reduce data variability caused during sampling, a series of quality-control samples should be utilized.

Replicate samples are important for the quality control of diffusion-sampler data. Sample replicates provide information needed to estimate the precision of concentration values determined from the combined sample-processing and analytical method and to evaluate the consistency of quantifying target VOCs. A replicate sample for water-filled diffusion samplers consists of two separate sets of VOC vials filled from the same diffusion sampler. Each set of VOC vials should be analyzed for comparison. Approximately 10 percent of the samplers should be replicated.

The length of the PDB sampler can be adjusted to accommodate the data-quality objectives for the sampling event. The length can be increased if additional volume is required for collection of replicate and matrix spike/matrix spike duplicate samples.

Trip blanks are used to determine whether external VOCs are contaminating the sample due to bottle handling and/or analytical processes not associated with field processing. Trip blanks are water-filled VOA vials prepared offsite, stored and transported with the other bottles used for collecting the environmental sample, and then submitted for analysis with the environmental sample. Consideration also should be given to the collection of a predeployment PDB trip blank to determine if the PDB samplers are exposed to extraneous VOCs prior to deployment. The predeployment trip blank should be a PDB sampler that is stored and transported with the field PDB samplers from the time of sampler construction to the time of deployment in the wells. An aliquot of the predeployment blank water should be collected from the PDB sampler in a VOA vial and submitted for analysis at the time of sampler deployment.

Water used to construct the diffusion samplers should be analyzed to determine the presence of background VOCs. Although many VOCs accidentally introduced into the diffusion-sampler water probably will reequilibrate with surrounding water once the diffusion samplers are deployed, some VOCs may become trapped within the diffusion-sampler water. For example, acetone, which is a common laboratory contaminant, does not easily move through the polyethylene diffusion samplers (Paul Hare, General Electric Company, oral commun., 1999). Thus, acetone inadvertently introduced into the diffusion-sample water during sampler construction may persist in the samplers, resulting in a false positive for acetone after sampler recovery and analysis.

Consideration should be given to the collection of a PDB trip blank to determine if the PDB samplers are exposed to extraneous VOCs prior to deployment. A trip blank is collected from a PDB sampler that is stored and transported with the field PDB samplers between the time of sampler construction and deployment in the well. The water for the trip blank is collected from the PDB sampler in VOA vials at the time of sampler deployment.

SUMMARY

Water-filled passive diffusion bag (PDB) samplers described in this report are suitable for obtaining a variety of VOCs in ground water at monitoring wells. The suggested application for PDB samplers is for long-term monitoring of VOCs in ground-water wells at well-characterized sites. Where the screened interval is greater than 10 ft, the potential for contaminant stratification and/or intra-borehole flow within the screened interval is greater than in screened intervals shorter than 10 ft. It is suggested that the vertical distribution of contaminants be determined in wells having 10-ft-long well screens, and that both the vertical distribution of contaminants and the potential for intra-borehole flow be determined in wells having screens longer than 10 ft. A typical PDB sampler consists of a 1- to 2-ft-long low-density polyethylene lay-flat tube closed at both ends and containing deionized water. The sampler is positioned at the target horizon by attachment to a weighted line or fixed pipe.

The amount of time that the samplers should be left in the well prior to recovery depends on the time required by the PDB sampler to equilibrate with ambient water and the time required for environmental disturbances caused by sampler deployment to return to ambient conditions. The rate that water within the PDB sampler equilibrates with ambient water depends on multiple factors, including the type of compound being sampled and the water temperature. Concentrations of benzene, *cis*-1,2-dichloroethene, tetrachloroethene, trichloroethene, toluene, naphthalene, 1,2-dibromoethane, and total xylenes within the PDB samplers equilibrated with the concentrations in an aqueous mixture of those compounds surrounding the samplers under laboratory conditions within approximately 48 hours at 21 °C. A subsequent laboratory study of mixed VOCs at 10 °C showed that tetrachloroethene and trichloroethene were equilibrated by about 52 hours, but other compounds required longer equilibration times. Chloroethane, *cis*-1,2-dichloroethene, *trans*-1,2-dichloroethene, and 1,1-dichloroethene were not equilibrated at 52 hours, but appeared to be equilibrated by the next sampling point at 93 hours. Vinyl chloride, 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,1-dichloroethane were not equilibrated at 93 hours but were equilibrated by the next sampling point at 166 hours. Different equilibration times may exist for other compounds. Differences in equilibration times, if any, between single-solute or mixed-VOC solutions have not yet been thoroughly examined.

The samplers should be left in place long enough for the well water, contaminant distribution, and flow dynamics to restabilize following sampler deployment. Laboratory and field data suggest that 2 weeks of equilibration probably is adequate for many applications. Therefore, a minimum equilibration time of 2 weeks is suggested. In less permeable formations, longer equilibration times may be required. When deploying PDB samplers in waters colder than previously tested (10 °C) or for compounds without sufficient corroborating data, a side-by-side comparison with conventional methodology is advisable to justify the field equilibration time.

Following the initial equilibration period, the samplers maintain equilibrium concentrations with the ambient water until recovery. Thus, there is no specified maximum time for sampler recovery after initial equilibration. PDB samplers have routinely been left in ground waters having concentrations of greater than 500 ppm of TCE for 3 months at a time with no loss of

bag integrity, and at one site, the PDB samplers were left in place in VOC-contaminated ground water for 1 year with no reported loss of sampler integrity. The effects of long-term (greater than 1 month) PDB-sampler deployment on sampler and sample integrity have not yet been thoroughly tested for a broad range of compounds and concentrations. In some environments, development of a biofilm on the polyethylene may be a consequence of long-term deployment. Investigations of semipermeable membrane devices (SPMDs) have shown that the transfer of some compounds across a heavily biofouled polyethylene membrane may be reduced, but not stopped. If a heavy organic coating is observed on a PDB sampler, it is advisable to determine the integrity of the sample by comparing sampler results to a conventional sampling method concentrations before continuing to use PDB samplers for long-term deployment in that well.

PDB methodology is suitable for a broad variety of VOCs, including chlorinated aliphatic compounds and petroleum hydrocarbons. The samplers, however, are not suitable for inorganic ions and have a limited applicability for non-VOCs and for some VOCs. For example, although methyl-*tert*-butyl ether and acetone and most semivolatile compounds are transmitted through the polyethylene bag, laboratory tests have shown that the resulting concentrations were lower than in ambient water. The samplers should not be used to sample for phthalates because of the potential for the LDPE to contribute phthalates to the water sample.

When attempting to determine whether the use of PDB samplers is appropriate at a particular well, a common approach is to do a side-by-side comparison with a conventional sampling method. This approach is strongly suggested in wells having temporal concentration variability. In a well having relatively low temporal concentration variability, comparison of the PDB-sampler results to historical concentrations may provide enough information to determine whether the PDB samplers are appropriate for the well. In general, if the two approaches produce concentrations that agree within a range deemed acceptable by the local, state, and Federal regulatory agencies, then use of a PDB sampler in that well will provide VOC concentrations consistent with the historical record. If concentrations from the PDB sampler are higher than concentrations from the conventional method, then it is probable that the concentrations from the PDB sampler are an adequate representation of ambient conditions. If, however, the conventional method produces concentrations

that are substantially higher than the concentrations found by using the PDB sampler, then the PDB sampler may or may not adequately represent local ambient conditions. In this case, the difference may be due to a variety of factors, including mixing or translocation due to hydraulic and chemical heterogeneity of the aquifer within the screened or open interval of the well and the relative permeability of the well screen.

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VROBLESKY

USER'S GUIDE FOR POLYETHYLENE-BASED PASSIVE DIFFUSION BAG SAMPLERS TO OBTAIN VOLATILE ORGANIC
COMPOUND CONCENTRATIONS IN WELLS

PART 1: DEPLOYMENT, RECOVERY, DATA INTERPRETATION,
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PART 2: FIELD TESTS

Water-Resources Investigations Report 01-4061

Prepared in cooperation with the

U.S. AIR FORCE

U.S. NAVAL FACILITIES ENGINEERING COMMAND

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User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells

Part 2: Field Tests

By Don A. Vroblesky, editor

U.S. Geological Survey

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Columbia, South Carolina
2001

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Conversion Factors, Vertical Datum, Acronyms, and Abbreviations

Multiply	By	To obtain
<i>Length</i>		
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
<i>Area</i>		
square mile (mi ²)	2.590	square kilometer
<i>Flow</i>		
foot per day (ft/d)	0.3048	meter per day
foot squared per day (ft ² /d)	0.09294	meter squared per day
gallons per minute (gal/min)	0.06308	liter per second
gallons per day (gal/d)	0.003785	cubic meter per day
inches per year (in/yr)	25.4	millimeters per year
<i>Volume</i>		
gallon (gal)	3.785	liter

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:
 $^{\circ}\text{F} = 9/5 (^{\circ}\text{C}) + 32$

Sea level refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Chemical concentration in water is expressed in metric units as milligrams per liter (mg/L) or micrograms per liter (µg/L).

Additional Abbreviations	
ft ³ /d	cubic feet per day
ft ³ /mg	cubic feet per milligram
g	gram
L	liter
µg	microgram
µm	micrometer
µL	microliter
mg	milligram
mL	milliliter
mL/min	milliliter per minute

User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells

Part 2: Field Tests

By Don A. Vroblesky, *editor*

INTRODUCTION

This report presents six case studies where passive diffusion bag (PDB) samplers were tested under field conditions. The sites represent two U.S. Naval facilities [Naval Air Station (NAS) North Island, California; and Naval Industrial Reserve Ordnance Plant (NIROP) Fridley, Minnesota], and three U.S. Air Force facilities [Davis Global Communications, California; Hanscom Air Force Base (AFB), Massachusetts; and McClellan AFB, California]. The primary ground-water contaminants of interest were chlorinated hydrocarbons. Two independent studies included herein were done at McClellan AFB (Tunks and others, 2000; McClellan AFB Environmental Management Directorate, 2000). Because of the length of the McClellan AFB Environmental Management Directorate (2000) study, only a summarization of the report is included herein. The detailed report is available from McClellan AFB Environmental Management Directorate, 5050 Dudley Boulevard, Suite 3, McClellan AFB, California, 95652-1389.

Most of the case studies are previously published reports or summaries of previously published reports, some of which are authored by non-U.S. Geological Survey personnel. Therefore, the formatting of the individual reports varies, and not all formats are standard for the U.S. Geological Survey. Moreover, the methods used for these investigations preceded publication of standardized approaches for using PDB samplers in wells. Therefore, investigators should refer to Part 1 of this document for guidance on recommended methodology for PDB sampler applications, rather than to the case studies presented here.

PDB-sampler methodology was compared to conventional purging methods (purging at least three casing volumes) used at McClellan AFB and Davis Global Communications, and to low-flow methods used at NAS North Island and Hanscom AFB. Both conventional purging and low-flow purging were compared with using PDB samplers at NIROP Fridley. The study by Tunks and others at McClellan AFB compared the PDB samplers to conventional and low-flow techniques, as well as another type of diffusion device, the DMLS sampler.

The sites showed close correspondence between concentrations obtained by the PDB samplers and concentrations obtained by using other techniques at most tested locations. Most of the field studies also reported some disagreement between results from the PDB samplers and results from the comparative method at a few wells. The places where disagreements between results were observed are of interest because they illustrate differences between the sources of water for each type of sampling method. For example, in a well at Davis Global Communications where concentrations from the PDB samplers were lower than from the conventional purge, heat-pulse flowmeter testing was used to show that the water from the purged sampling probably was transported downward from a shallower contaminated aquifer during the well purge. When the well was not being pumped, however, the greatest amount of water entering the screen was from the sand layer adjacent to the screen. The data suggest that the PDB samplers provided concentrations characteristic of the aquifer under normal circumstances, whereas the pumped sample represented a mixture of water from the near vicinity of the well

screen, as well as contaminated water from a shallower horizon. Although the two methods did not agree, it appears that the PDB samplers provided results more characteristic of the aquifer adjacent to the screened interval.

Typically, other field studies also found that concentration differences between the PDB samplers and the pumping methodology used for comparison often could be attributed to an obscuring of the contaminant stratification by the mixing of water during pumping. Field evidence to support this hypothesis is shown in the reports on NAS North Island, Hanscom AFB, McClellan AFB, and NIROP Fridley. In general, the data show that even when the results of the PDB sampling and the conventional or low-flow-purging approaches disagree, the results of the PDB sampling often appear to accurately reflect the local concentrations, whereas those of the pumped sampling method reflect a mixing.

The investigation at McClellan AFB by Tunks and others, included in this report, shows a cost comparison for various sampling methods, however, some of these costs include a one-time investment for

the field test. Cost savings from more standard well-monitoring activities have been reported to range from 25 to 70 percent (Alexander and Lammons, 1999; Hare, 2000; U.S. Army Corps of Engineers, 2000; Brian Peters, OHM Remediation Services Corp., written commun., 2000). Cost savings of PDB sampling over conventional three-casing-purge sampling are described in the McClellan AFB Environmental Management Directorate report (2000), however, calculation errors obscure the actual amount of the savings.

Due to the availability of reports at the time of publication, the case studies included herein are limited to applications at sites where chlorinated aliphatic hydrocarbons are the primary contaminants. The case studies present data suggesting that PDB samplers can provide representative concentrations of the target compounds in a variety of environments. The method is a cost-effective, simple alternative to traditional sampling methodologies.

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Diffusion Sampler Evaluation of Chlorinated VOCs in Groundwater

By John Tunks, Peter Guest, and Javier Santillan

Diffusion Sampler Evaluation of Chlorinated VOCs in Groundwater

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ABSTRACT: Groundwater sample collection using diffusion samplers represents a relatively new technology that utilizes passive sampling methods for monitoring volatile organic compounds (VOCs) in groundwater. The potential benefits and cost savings of diffusion sampler use as an instrument for long-term monitoring are significant, as no purge waters are generated, and labor requirements for sampler installation and retrieval are minimal. The efficacy of diffusion samplers for evaluating chlorinated VOCs in groundwater was assessed. Using two types of diffusion samplers, groundwater samples were collected at discrete depths to assess vertical contamination profiles. Groundwater samples also were collected following low-flow/minimal drawdown purging and conventional purging techniques. Results obtained using the various sampling techniques suggest that the diffusion samplers provide comparable accuracy with and can be significantly less expensive than traditional sampling techniques.

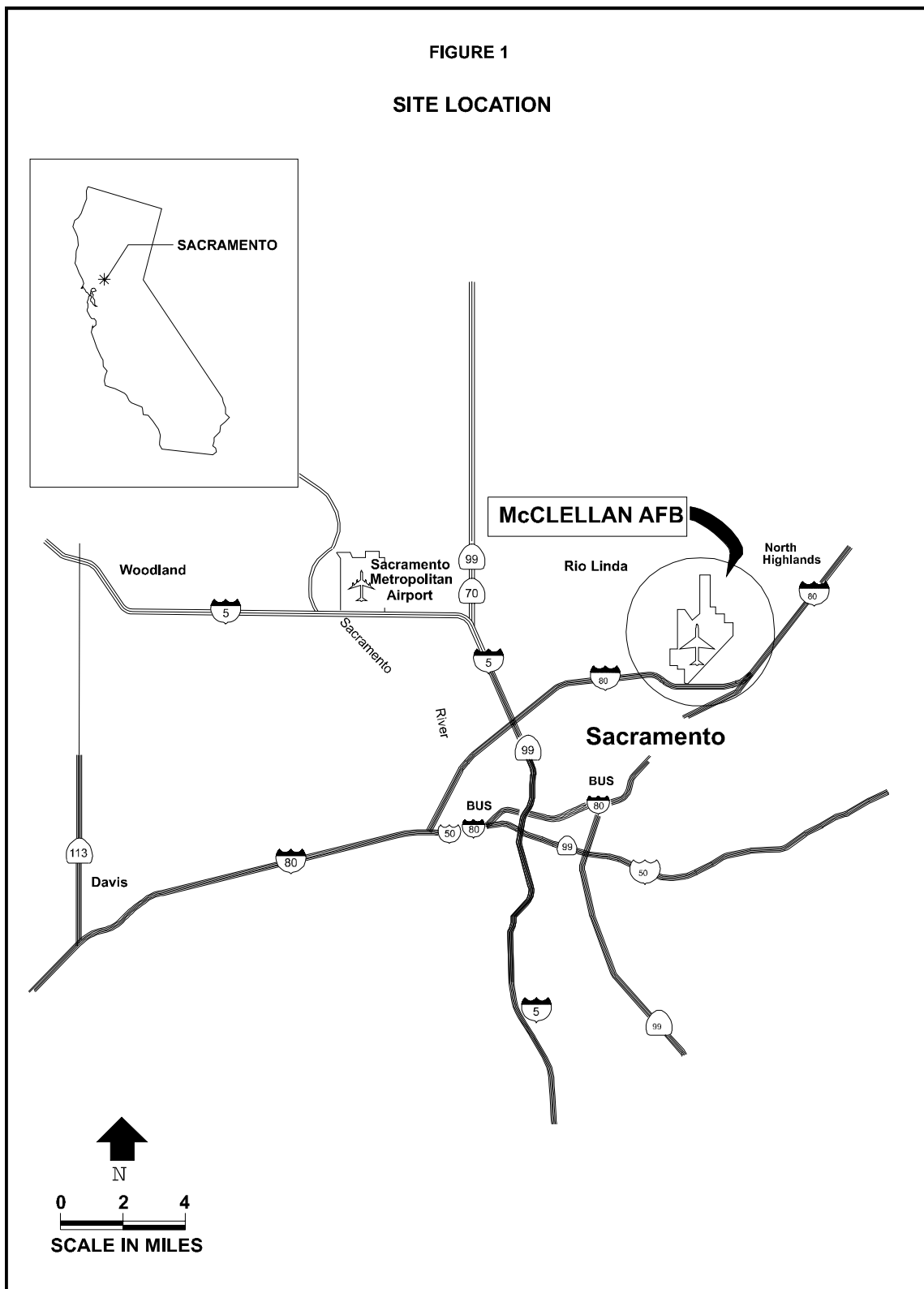
INTRODUCTION

Parsons Engineering Science, Inc. (Parsons ES) was retained by the US Air Force Center for Environmental Excellence, Technology Transfer Division (AFCEE/ERT) to perform an evaluation of passive groundwater diffusion sampling technology. The diffusion sampler evaluation is part of the AFCEE/ERT Remedial Process Optimization (RPO) demonstration project being performed at six Air Force bases (AFBs) nationwide. One of these bases, McClellan AFB, California (figure 1), was selected as the site for this evaluation. A field study was performed in August 1999 at a site on McClellan AFB where deep groundwater, more than 30 meters below ground surface, is contaminated with various chlorinated VOCs as a result of solvent disposal into burn pits during the 1940s through 1970s.

The objective of the diffusion sampler evaluation was to evaluate the efficacy of this groundwater sampling method relative to standard sampling methods. Field sampling was conducted using two types of diffusion samplers to collect groundwater samples from varying depths at selected monitoring wells. The diffusion samplers evaluated included the commercially available DMLS™ sampler (obtained from Johnson Screens, New Brighton, Minnesota in August 1999), and a sampler currently being developed and used by the US Geological Survey (USGS). The standard sampling methods used for comparison to the diffusion sampling results were:

1. Groundwater sampling following conventional purging of at least 3 casing-volumes of water and stabilization of water quality parameters (i.e., conventional sampling); and
2. Sampling following low-flow/minimal drawdown purging (i.e., micropurging). The groundwater samples were analyzed for total VOCs using US Environmental Protection Agency (USEPA) Method SW8260B/5030 (USEPA, 1994).

FIGURE 1
SITE LOCATION

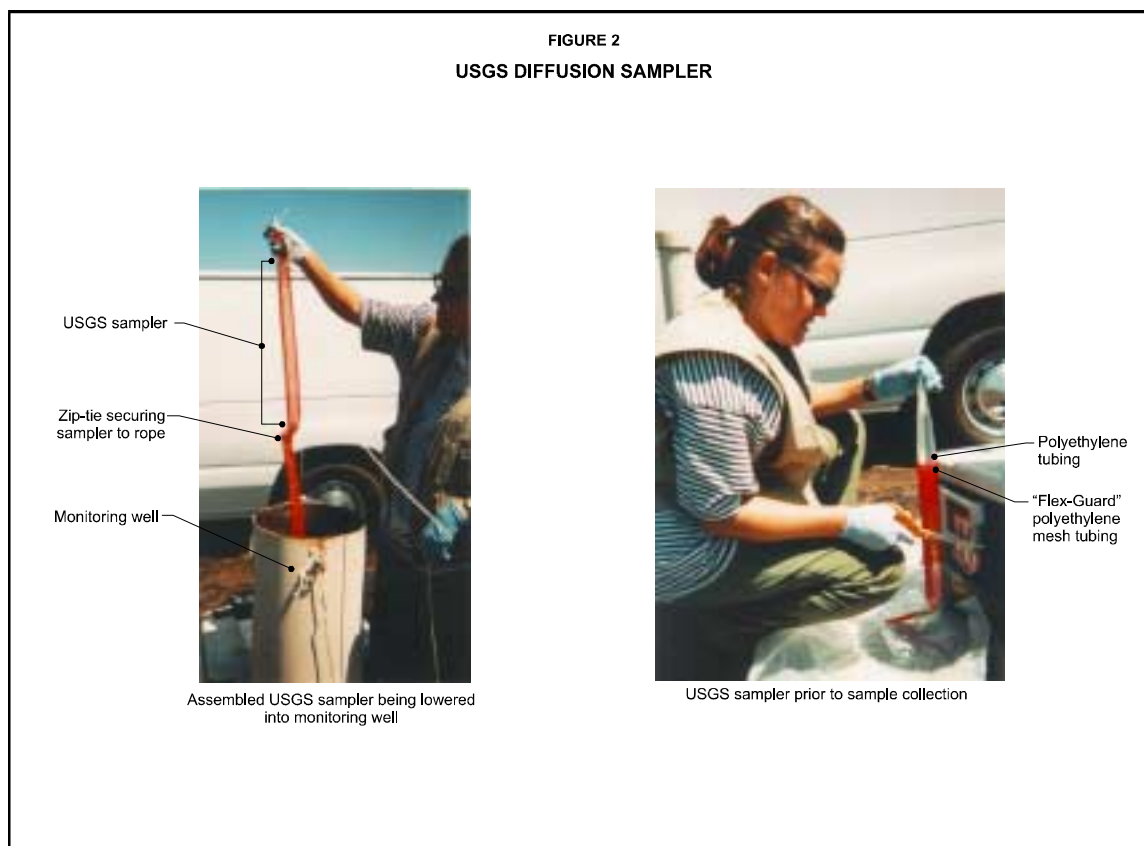


MATERIALS AND METHODS

Diffusion sampling is a relatively new technology designed to use passive sampling techniques that eliminate the need for well purging. A diffusive-membrane capsule is filled with deionized distilled water, sealed, mounted in a suspension device, and lowered to a specified depth in a monitoring well. Over time (no less than 72 hours), VOCs in the groundwater diffuse across the capsule membrane, and contaminant concentrations in the water inside the sampler attain equilibrium with the ambient groundwater. The sampler is subsequently removed from the well, and the water within the diffusion sampler is transferred to a sample container and submitted for analysis. The diffusive membranes evaluated in this study are rated for VOCs only. These membranes are not appropriate for monitoring larger or more electrically charged molecules.

Once a diffusion sampler is placed in a well, it remains undisturbed until equilibrium is achieved between the water in the well casing and the water in the diffusion sampler. Depending on the hydrogeologic characteristics of the aquifer, the diffusion samplers can reach equilibrium within 3 to 4 days (Vroblesky and Campbell, 1999); however for this evaluation, a minimum 14-day equilibrium period was used. Groundwater samples collected using the diffusion samplers are thought to be representative of water present within the well during the previous 24 to 72 hours.

USGS Sampler.—The standard USGS diffusion sampler, shown in figure 2, consists of water-filled, low-density polyethylene tubing, which acts as a semi-permeable membrane. The USGS sampler typically is constructed of a 45-centimeter (cm)-long section of 5.08-cm-diameter, 4-mil polyethylene tubing that is heat-sealed on both ends. The sampler holds approximately 300 milliliters (mL) of deionized distilled water. A longer 7.62-cm-diameter sampler that holds approximately 500 mL of water also is available if larger sample volumes are required. The sampler is placed in “flex-guard” polyethylene mesh tubing for abrasion protection, attached to a weighted rope, and lowered to a predetermined depth within the screened interval of a well. The rope is weighted to ensure that the sampling devices are positioned at the correct depth and that they do not float upward through the water column.



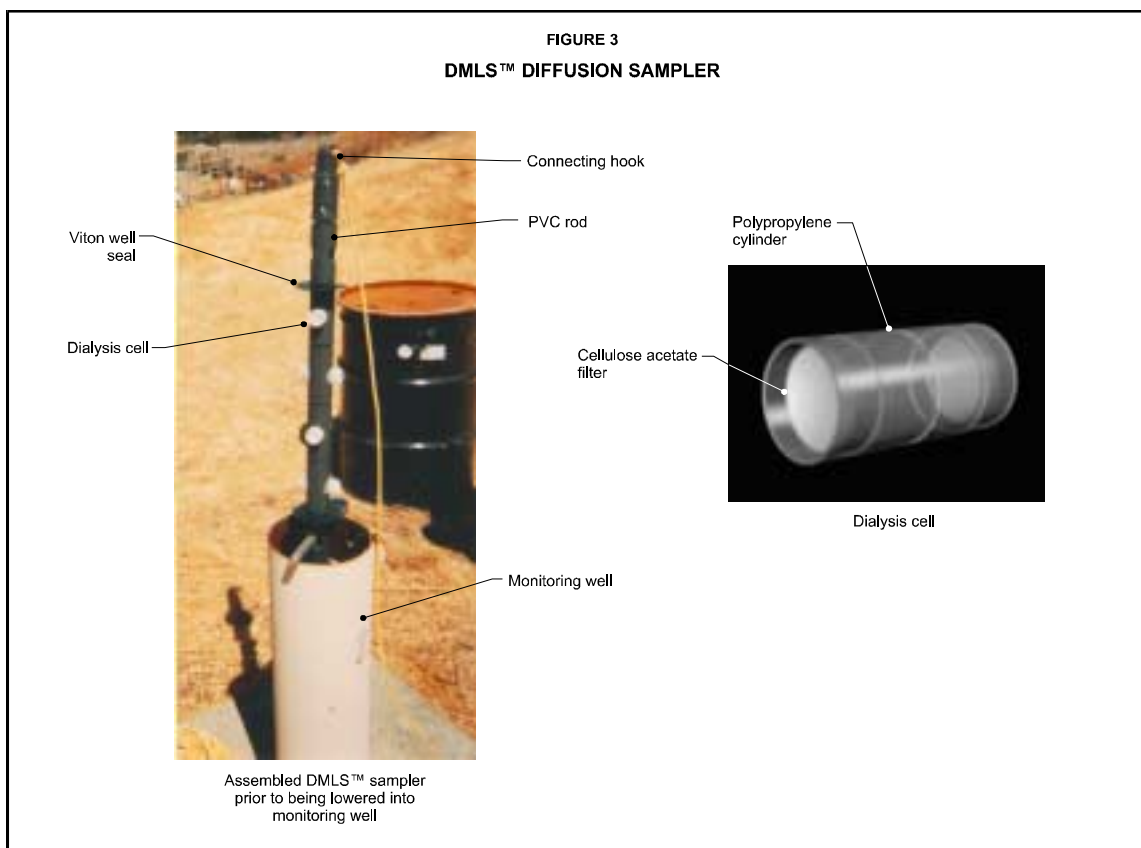
For this evaluation, multiple USGS samplers were placed end-to-end in three test monitoring wells to develop vertical contamination profiles. Upon recovery, the samplers were cut open, and water samples were transferred into 40-mL volatile organics analysis (VOA) vials. The samples were preserved and submitted for analysis.

DMLSTM Sampler.—The DMLSTM™ sampler, shown in figure 3, uses dialysis cells as passive collection devices. The dialysis cells are composed of a polypropylene cylinder that holds 38 mL of deionized distilled water. The cells have 0.2-micrometer cellulose acetate filters attached to each end of the cell that serve as the permeable membranes. The cells are mounted in cylindrical holes pre-drilled through a 152-cm-long polyvinyl chloride (PVC) rod, and are separated by viton spacers, or well seals, that fit the inner diameter of the well. The PVC rod can accommodate as many as 12 sampling cells (pre-drilled cylindrical hole spacing is 12.7 cm), and a string of up to 5 rods can be connected together for sampling over long screened well intervals.

Once loaded with the prepared dialysis cells, the PVC rods are lowered into a well to the desired depth within the screened interval, and are secured with a rope to the top of the well casing. A stainless steel weight is attached to the bottom of the deepest PVC rod to ensure that the samplers are positioned at the correct depth in the well, and that the PVC rods do not float through the water column.

Upon retrieval of the PVC rods, the dialysis cells are removed from the PVC rod, emptied into a decontaminated container for compositing, and then transferred to 40-mL VOA containers. The samples are preserved and sent to a laboratory for analysis.

Conventional Sampling.—Groundwater sampling using conventional well purging involves removing a large volume of water (3 to 5 well casing-volumes) from the well over a short time. The objective of conventional purging is to remove all water present within the well casing, as well as groundwater present in the surrounding well filter pack. Theoretically, by removing this water quickly, the “stagnant” water that resided in the well and filter



pack will be replaced with “fresh” groundwater from the surrounding formation with minimal mixing. The “fresh” groundwater that is then sampled is considered to be representative of the local groundwater. Rapid drawdown of the water level in a well is not uncommon, and often wells are purged dry using this method. Conventional purging is frequently performed using a bailer or a high-flow submersible pump (e.g., Grundfos Redi-Flo2 pump).

Micropurging.—The objective of micropurging is to remove a small volume of water at a low flow rate from a small portion of the screened interval of a well without mixing water among vertical zones. Ideally, by placing the inflow port of a pump at a prescribed depth within the screened interval of a well, and by withdrawing water at a slow rate, groundwater will be drawn from the aquifer into the well only in the immediate vicinity of the pump. This discrete-depth sampling allows for vertical definition of contamination in the aquifer. The pumping rate is adjusted to minimize drawdown. Because micropurging relies on a pumping rate that does not exceed the natural groundwater recharge rate, the water elevation in the well must be monitored to ensure that drawdown does not occur.

Field Activities.—Three monitoring wells were selected for use in this evaluation. In each of the wells, a maximum of three depth intervals spaced equally across the well screen were monitored using the different sampling methods. Using the two types of diffusion samplers as designed, it was necessary to perform the diffusion sampling consecutively, as samples from the two types of diffusion samplers could not be collected concurrently from the same interval within a well. To evaluate the potential changes in groundwater concentrations over the sampling periods (approximately 14 days between diffusion sampler collection events), conventional groundwater sampling was performed following completion of each diffusion sampling event. Significant differences in groundwater chemistry measured between the two sampling events could be normalized using the two sets of conventional groundwater data.

RESULTS AND DISCUSSION

Of the 67 analytes included in the SW8260B analysis, 17 were reported to have detectable concentrations in at least one of the samples submitted for analysis. For the purposes of comparing the analytical accuracy or comparability using the different sampling methods, only those analytes that were detected in at least 10 samples were considered in this study. These analytes include trichloroethene (TCE), *trans*-1,2-dichloroethene (DCE), *cis*-1,2-DCE, 1,1-DCE, 1,1-dichloroethane (DCA), 1,2-DCA, and 1,1,2-trichloroethane (TCA). A summary of analytical results for these analytes is presented in table 1.

The different methods of sample collection were evaluated using the following criteria: accuracy or comparability of data, other method-specific criteria, and cost. These criteria are described in the following sections.

Accuracy/Comparability of Data.—The analysis-of-variance (ANOVA) test was used to compare analytical data collected using the different sampling techniques. The limited number of samples available (as few as 3 per sampling method) precluded the use of linear statistical models in a quantitative manner. Therefore, the ANOVA was used in a qualitative manner to provide a “weight-of-evidence” support for data accuracy and similarity.

The ANOVA test returns a “p-value” between zero and one, indicating a “pass” or “fail” condition. A p-value of 0.05 or greater represents a pass, indicating that the distributions are similar at the 95-percent confidence level.

ANOVA is a parametric test, and it is common practice to verify that the data fit a parametric distribution prior to applying the tests. However, due to the limited number of samples in the data set, normality tests were not performed on the data sets before performing the ANOVA.

In instances where a nondetectable concentration of an analyte was reported for a sample, a value of zero was assigned for the purposes of the ANOVA testing only. For the conventional purging, each of the three depth intervals evaluated was assigned the same analytical value reported for the one sample collected from that well.

Table 1. Analytical results for samples

[µg/L, micrograms per liter]

Well ID	First Mobilization			Second Mobilization	
	USGS	Micropurge	Conventional	DMLS™	Conventional
TCE (µg/L)					
MW11	8 to 23	24	29	8 to 10	21
MW241	3.8 to 40	27 to 33	41	27 to 33	32
MW242	3.4 to 6	2.8 to 3.5	4	3.3 to 5.3	3.1
<i>trans</i>-1,2-DCE (µg/L)					
MW11	ND	ND	ND	ND	ND
MW241	ND to 1.2	0.90 to 0.98	1	0.77 to 1.4	0.99
MW242	ND	ND	ND	ND	ND
<i>cis</i>-1,2-DCE (µg/L)					
MW11	0.95 to 2.3	3.4	3.8	1.1 to 1.4	3.3
MW241	0.63 to 9.2	6.5 to 7.2	7.2	6 to 11	6.8
MW242	ND	ND	ND	ND	ND
1,1-DCE (µg/L)					
MW11	34 to 89	170	220	58 to 77	170
MW241	2.1 to 22	15 to 19	23	19 to 21	18
MW242	4.4 to 9	3.8 to 6.3	5.4	5.2 to 10	3.1
1,1-DCA (µg/L)					
MW11	0.66 to 1.6	1.6	1.7	0.54 to 0.69	1.5
MW241	0.36 to 4.4	3.5 to 3.6	3.6	2.9 to 4.3	3.4
MW242	ND	ND	ND	ND to 0.22	ND
1,1,2-TCA (µg/L)					
MW11	0.58 to 1.6	1.3	1.6	0.47 to 0.68	1.5
MW241	0.32	0.23 to 0.28	0.32	0.22 to 0.27	0.27
MW242	ND	ND	ND	ND	ND
1,2-DCA (µg/L)					
MW11	0.95 to 2.2	2.2	2	0.74 to 0.83	1.9
MW241	1.8 to 16	14 to 16	15	12 to 15	15
MW242	0.43 to 1.6	0.98 to 3.5	5.3	0.78 to 1.4	3.6

Notes:

“8 to 23” – Range of concentrations measured over sampled depth intervals.

ND – Not detected.

Data validation qualifiers did not affect the usability of the data for this evaluation and are therefore not included in table 1.

As presented in table 2, in all instances the p-values calculated for the populations of results for the different sampling methods exceeded 0.05. These ANOVA results indicate that there are no statistically significant differences among analytical results obtained using the four groundwater sampling techniques. Given that the evaluated diffusion samplers provide comparable accuracy with traditional sampling techniques, other criteria must be considered in evaluating the suitability of one sampling technique over another.

Table 2. ANOVA results

Analyte	p-value
1,1,2-TCA	0.74
1,1-DCA	0.99
1,1-DCE	0.47
1,2-DCA	0.88
cis-1,2-DCE	0.96
TCE	0.59
trans-1,2-DCE	0.99

Other Method-Specific Criteria.—Additional qualitative and semi-quantitative criteria were considered in this evaluation and are summarized in table 3.

Table 3. Summary of other method-specific criteria results

Criteria	USGS	DMLS™	Micropurge	Conventional
Ease of use	Excellent	Fair	Poor	Fair
Labor hours required per sample	0.66	1	2.75	3.66
Generation of IDW (liters)	< 1	< 1	100	500
Cost to provide dedicated equipment in each well	Low	High	Low	High
Decontamination required if dedicated equipment is not used	Minimal	High	Moderate	Moderate
Immediacy of sample availability	Slow	Slow	Rapid	Rapid
Can analytes other than VOCs be monitored?	No	No	Yes	Yes
Can vertical distribution of contaminants be evaluated?	Possible	Possible	Partial	No
Suitable for natural attenuation monitoring?	No	No	Yes	Partial

Supplemental to the criteria shown in table 3, concerns specific to the USGS and DMLS™ samplers were noted. Being placed in a well for potentially long periods, these samplers are susceptible to the effects of fluctuating groundwater elevations. If groundwater elevations decrease such that a portion of the diffusion sampler is exposed to air, the potential exists for volatilization of VOCs, which would compromise the samples collected from these devices.

A second concern was identified with the DMLS™ sampling device in that the sample volume of each dialysis cell is only 38 mL. When collecting samples for VOC analysis, the typical sample container is a 40 mL VOA, which will require more than one dialysis cell to fill.

As shown in table 3, many benefits can be realized through the use of diffusion samplers, however these devices also present limitations which may preclude their use in certain groundwater sampling applications.

Cost.—Cost estimates per sample for each of the four sampling methods evaluated are presented in table 4. The following expenses were considered in the development of a cost analysis for each different sampling method: labor, equipment, and disposal or management of investigation-derived waste (IDW). Some of the costs involved in these activities are one-time expenses that are not incurred each time a sample is collected (e.g., PVC rods for use with the DMLS™ samplers and stainless steel weights). Furthermore, labor and material costs can vary depending on the scope of the sampling event (e.g., it is less expensive on a unit-cost basis to collect 100 samples than to collect 5 samples). However, to present the most accurate estimate of costs associated with this evaluation, only the costs incurred during this field study were considered in the cost analysis. Labor costs were based on actual hours expended as documented in the field notes and the burdened labor rate for a typical field scientist. Equipment costs were taken directly from invoices (when available) or were estimated from vendor quotes. Costs associated with disposal or management of IDW can vary widely depending on the approach used. For this analysis, the only costs considered in the management of IDW are those dealing with containerizing the waste.

Table 4. Cost summary

Sampling technique	Cost per sample
USGS	\$65
DMLS™	\$555
Micropurge	\$308
Conventional	\$444

As noted, these costs are approximated based on the limited scope of this investigation. If these sampling technologies were applied to large-scale monitoring programs, a reduction in the per-sample cost would probably be realized due in part to reusable equipment that is associated with some of the sampling methods.

As shown in table 4, the cost per sample using the USGS diffusion sampler was substantially less than using any other methods. Conversely, the DMLS™ sampler per sample cost was substantially more than any other method.

CONCLUSIONS

The Air Force groundwater diffusion sampler evaluation indicates that diffusive sampling technology can be a cost-effective and accurate method for environmental groundwater monitoring of VOCs. However, use of diffusion samplers may not be appropriate for all applications. Of the diffusion sampling technologies evaluated, the USGS sampler is the recommended device based on the evaluation criteria presented herein. Additional comparisons between the different sampling technologies should be performed to develop a more robust data set upon which to base analytical result comparisons. Particularly, varying hydrogeologic settings (e.g., low-permeability to high-permeability aquifers) and increasing the number of wells in the evaluation would allow for more thorough evaluation of the comparability of the analytical data.

If natural attenuation monitoring is required, a combination of sampling techniques should be considered. For instance, annual monitoring of natural attenuation parameters can be performed using a traditional sampling method, while quarterly monitoring of VOCs can be accomplished using diffusion sampling technology.

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Diffusion Sampler Testing at Naval Air Station North Island, San Diego
County, California, November 1999 to January 2000
USGS Water-Resources Investigations Report 00-4182

By Don A. Vroblesky and Brian C. Peters

Diffusion Sampler Testing at Naval Air Station North Island, San Diego County, California, November 1999 to January 2000

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ABSTRACT

Volatile organic compound concentrations in water from diffusion samplers were compared to concentrations in water obtained by low-flow purging at 15 observation wells at the Naval Air Station North Island, San Diego, California. Multiple diffusion samplers were installed in the wells. In general, comparisons using bladder pumps and diffusion samplers showed similar volatile organic carbon concentrations. In some wells, sharp concentration gradients were observed, such as an increase in *cis*-1,2-dichloroethene concentration from 100 to 2,600 micrograms per liter over a vertical distance of only 3.4 feet. In areas where such sharp gradients were observed, concentrations in water obtained by low-flow sampling at times reflected an average concentration over the area of influence; however, concentrations obtained by using the diffusion sampler seemed to represent the immediate vicinity of the sampler. When peristaltic pumps were used to collect ground-water samples by low-flow purging, the volatile organic compound concentrations commonly were lower than concentrations obtained by using diffusion samplers. This difference may be due to loss of volatiles by degassing under negative pressures in the sampling lines induced while using the peristaltic pump, mixing in the well screen, or possible short-circuiting of water from an adjacent depth. Diffusion samplers placed in buckets of free-phase jet fuel (JP-5) and Stoddard solvent from observation wells did not show evidence of structural integrity loss during the 2 months of

equilibration, and volatile organic compounds detected in the free-phase fuel also were detected in the water from the diffusion samplers.

INTRODUCTION

Low-density polyethylene diffusion samplers, filled with deionized water or air, have been shown to be an inexpensive alternative sampling method for volatile organic compounds (VOCs) in contaminated wells or in ground-water discharge zones beneath surface-water bodies (Vroblesky and others, 1996; Vroblesky and Robertson, 1996; Vroblesky and Hyde, 1997; Vroblesky and others, 1999; Gefell and others, 1999). The use of diffusion samplers in wells has generated substantial interest due to their capability to sample ground water without the need for prior well purging.

The Naval Air Station (NAS) North Island, in San Diego County, California, has been used since 1917 as an air station, harbor, and training base. The base is approximately 1 mile west across San Diego Bay from the San Diego metropolitan area (fig. 1). Activities at the base have resulted in ground-water contamination by a variety of compounds, including chlorinated aliphatic hydrocarbons and petroleum hydrocarbons. In addition, free-phase JP-5 jet fuel and Stoddard solvent (mineral spirits) are present locally in the ground water. Stoddard solvent is a refined petroleum product typically used as a thinning agent for paints, coatings, waxes, printing inks, and adhesives; a solvent in photocopy toners and in dry cleaning; and as a degreaser for engine parts.

The purpose of this report is to present the findings of an investigation to determine whether the use of polyethylene deionized-water-filled diffusion



Figure 1. Location of observation wells, Naval Air Station North Island, California.

samplers is a viable method of sampling VOCs in ground water at the base. VOC concentrations in water obtained from diffusion samplers set at multiple levels in wells are compared to VOC concentrations in water obtained from low-flow sampling. Diffusion samplers were placed in 15 observation wells, and 2 samplers were placed in buckets of free-phase JP-5 and Stoddard solvent.

Acknowledgments

The Department of the Navy, Southwestern Division Naval Facilities Command, funded this work. The fieldwork was a cooperative effort between the U.S. Geological Survey and OHM Remediation Services Corp.

METHODS

Diffusion samplers were tested in 15 wells at NAS North Island, California. VOC concentrations in water from the diffusion samplers were compared to VOC concentrations in water from low-flow sampling ports open adjacent to each diffusion sampler. Low-flow sampling was accomplished by using a peristaltic pump at most sites and a bladder pump at selected sites.

Diffusion-Sampler Construction and Deployment

Each diffusion sampler consisted of a 2-inch-diameter, low-density polyethylene (LDPE) tube heat-sealed at both ends and containing deionized water. On the outside of each sampler, an LDPE mesh provided abrasion protection. This sampling methodology is patented (patent number 5,804,743) and is available for non-exclusive licensing from the U.S. Geological Survey Technology Enterprise Office, Mail Stop 211, National Center, 12201 Sunrise Valley Drive, Reston, Virginia (telephone 703 648-4450; fax 703 648-4408).

Diffusion samplers were attached to intakes of bladder pumps by means of plastic cable ties. Attached to each remaining diffusion sampler was a Tygon tube extending from the sampler to land surface. The tubing was secured to the diffusion sampler and to a weighted line at approximately 10-foot intervals by using plastic cable ties. The purpose of the tubing was to allow ground water to be collected adjacent to each diffusion sampler by using low-flow methodology with a peristaltic pump.

The diffusion samplers were deployed in 15 wells at NAS North Island during November 11, 1999 (table 1). All wells were constructed of 4-inch-diameter casing. The samplers were attached by plastic cable ties to either a weighted line or a 1/2-inch (outside diameter) PVC pipe. When multiple sections of PVC pipe were required to reach the top of the casing, the sections were joined using stainless-steel screws. The PVC pipe was secured to the top of the well casing to prevent the diffusion samplers from shifting during the equilibration period.

Two of the sampled wells (PW-15 and PW-55) contained floating nonaqueous-phase liquid (LNAPL) consisting of free-phase petroleum and Stoddard solvent. To install diffusion samplers in these wells, a

Table 1. Summary of well information, Naval Air Station North Island, California

[ft, feet; ft bls, feet below land surface; ft msl, feet relative to mean sea level; Elev., elevation; NM, not measured; NA, not available; TOC, top of casing; A, bladder pump attached to the diffusion sampler; B, peristaltic pump using tubing attached to individual diffusion samplers; C, same as B, except one depth was sampled using a bladder pump attached to a diffusion sampler; D, same as B, except the well was resampled using a bladder pump following removal of the diffusion samplers]

Site or building designation	Well identifier	Depth to screen top(ft bls)	Depth to screen bottom (ft bls)	Saturated screen length (ft)	Depth to water (ft bls)	Elev. of water (ft msl)	Low-flow sampling method
653	MW-10	5	20.0	13.0	7.01	2.65	B
653	MW-13A	4	14.0	8.18	6.01	1.81	D
653	MW-13B	24.3	29.2	5.00	6.15	1.53	D
653	MW-13C	44.8	49.8	5.00	6.00	1.61	D
472	MW-68 C2	37	63.0	25.0	NM	NA	B
472	MW-68A	14	24.0	2.76	21.38	2.34	B
472	MW-68B	33	40.0	5.00	21.42	2.33	B
472	MW-68C	64.3	70.5	5.00	21.6	1.99	B
379	PW-15	20	35.0	9.94	23.34	2.61	B
379	PW-55	20	35.0	9.33	24.32	2.34	B
379	PW-66	20	35.0	10.0	25.10	2.40	B
Site 11	MW-12	30	39.7	13.7	NM	NA	C
Site 11	MW-5D	NA	60.0	35.5	NM	NA	C
Site 11	MW-9	23	31.9	4.10	28.18	5.64	A
Site 2	S2-MW-6A	5	20.0	14.3	5.64	2.35	B

rubber cap was placed on the lower end of a section of 2-inch-diameter PVC pipe and lowered into the well to a depth below the LNAPL. The top end of the pipe extended to land surface. A smaller diameter pipe then was used to pound out the rubber cap, which was recovered from the well along the outside of the 2-inch-diameter pipe by means of a rope attached to the cap. The diffusion samplers were lowered into the well through the 2-inch-diameter pipe, thereby avoiding direct contact with the LNAPL. The pipe was secured in place to allow the diffusion sampler to be recovered without contact with the LNAPL.

Collection of Pumped Ground-Water Samples

The diffusion samplers were allowed to remain undisturbed in the well water for 65 to 71 days (table 2). The wells were sampled at the time of sampler recovery using low-flow techniques. Low-flow sampling consisted of purging the well by means of using a dedicated bladder pump or a peristaltic pump connected to the Tygon tubing that had been attached to each of the diffusion samplers prior to deployment. Purging was done at a rate of 120 milliliters per minute until measurements of pH, water temperature, and specific conductance stabilized. In general, purging involved about 20 minutes of pumping and removal of less than 1 gallon of water from each sampling port. Decontamination of equipment was not required because each sampling interval had dedicated tubing.

A variety of methods were used to retrieve the diffusion samplers and to low-flow sample the well. The first method of sample retrieval involved recovering the diffusion sampler from the well immediately following low-flow sampling by using a bladder pump from the depth at which the diffusion sampler had equilibrated (well MW-9 only). A second method involved using a peristaltic pump to low-flow sample ground water adjacent to each of the diffusion samplers by means of the dedicated Tygon tubing attached to each diffusion sampler. The depths were low-flow sampled beginning with the shallowest and proceeding to the deepest. In some wells (MW-5 and MW-12), one of the depths was sampled using a dedicated bladder pump while the remaining depths were sampled using a bladder pump attached to dedicated tubing. Two wells (MW-13A and MW-13B) were low-flow sampled by using a peristaltic pump, the diffusion samplers were recovered, a bladder pump was inserted into each well, and the wells were then immediately

resampled by low-flow methodology using the bladder pump.

The diffusion samplers were recovered from the wells by means of the attached weighted line or PVC pipe. The samplers were cut open, and the water was slowly decanted into glass vials pretreated with hydrochloric acid. The water samples were sent to a contract laboratory for analysis by using Environmental Protection Agency Method 8260B (U.S. Environmental Protection Agency, 1999). Replicate samples were collected from approximately 10 percent of the sampling sites. In general, both diffusion samples and low-flow samples compared well with their respective replicate samples (tables 3 and 4).

RESULTS AND DISCUSSION

VOC concentrations in water obtained from diffusion samplers were similar to concentrations obtained by using low-flow sampling methods for most of the tested wells (tables 5 and 6, respectively). As will be shown, most concentration differences between the two sampling methods probably can be attributed to VOC degassing during peristaltic-pump sampling or to in-well mixing.

Comparison of Diffusion-Sampler Results to Bladder-Pump Results

Tests showing the most direct comparison between diffusion sampling and low-flow sampling were in wells where a bladder pump was used to low-flow sample. The test producing the least amount of well-water disturbance was in well MW-9 where a diffusion sampler was recovered immediately following low-flow sampling using a bladder pump from the same depth. Concentrations of 1,1-dichloroethene (1,1-DCE) and trichloroethene (TCE) obtained using the diffusion sampler agreed well (12 and 3 percent difference, respectively) with those obtained using the bladder pump (table 7). The difference is about the same as the differences (approximately 12 percent) in 1,1-DCE and TCE concentrations measured in replicate samples collected by using a dedicated bladder pump at well MW-5D (table 4). Thus, 12 percent is within the sample-collection variability for 1,1-DCE and TCE. Agreement between the methods was poorer for tetrachloroethene (PCE) concentrations. The PCE concentration in water from the diffusion sampler was 21 percent lower than the concentration in water

Table 2. Sampler deployment and recovery information, Naval Air Station North Island, California, November 1999 to January 2000

[repl, replicate sample; NA, not applicable; *, low-flow bladder-pump sample; #, data from OHM Remediation Services Corporation (2000)]

Site or building designation	Well identifier	Sampling interval identifier	Low-flow sample laboratory identifier	Diffusion-sampler laboratory identifier	Depth to diffusion-sampler center (ft bls)	Date installed	Date recovered	Number of days diffusion samplers were in wells
653	MW-10	A	779679-0091	779679-0099	7.75	11/12/99	1/18/00	67
653	MW-10	B	779679-0092	779679-0100	9.15	11/12/99	1/18/00	67
653	MW-10	C	779679-0093	779679-0101	11.1	11/12/99	1/18/00	67
653	MW-10	D	779679-0094	779679-0102	13.1	11/12/99	1/18/00	67
653	MW-10	E	779679-0095	779679-0103	15.1	11/12/99	1/18/00	67
653	MW-10	F	779679-0096	779679-0104	17.1	11/12/99	1/18/00	67
653	MW-10	G	779679-0097	779679-0105	18.8	11/12/99	1/18/00	67
653	MW-10	G repl	779679-0098	NA	18.8	11/12/99	1/18/00	67
653	MW-13A	A	779679-0030	779679-0042	6.50	11/10/99	1/17/00	68
653	MW-13A	B	779679-0031	779679-0043	7.95	11/10/99	1/17/00	68
653	MW-13A	C	779679-0032	779679-0044	9.35	11/10/99	1/17/00	68
653	MW-13A	D	779679-0033	779679-0045	10.9	11/10/99	1/17/00	68
653	MW-13A	E	779679-0034	779679-0046	12.4	11/10/99	1/17/00	68
653	MW-13A*#	NA	NA	NA	NA	NA	1/17/00	NA
653	MW-13B	A	779679-0035	779679-0047	24.8	11/10/99	1/17/00	68
653	MW-13B	B	779679-0036	779679-0048	26.1	11/10/99	1/17/00	68
653	MW-13B	C	779679-0037	779679-0049	27.5	11/10/99	1/17/00	68
653	MW-13B*#	NA	NA	NA	NA	NA	1/17/00	NA
653	MW-13C	A	779679-0038	779679-0054	45.4	11/10/99	1/17/00	68
653	MW-13C	B	779679-0039	779679-0055	46.6	11/10/99	1/17/00	68
653	MW-13C	B repl	779679-0041	NA	46.6	11/10/99	1/17/00	68
653	MW-13C	C	779679-0040	779679-0056	48.0	11/10/99	1/17/00	68
653	MW-13C*#	NA	NA	NA	NA	NA	1/17/00	NA
472	MW-68A	A	779679-0023	779679-0025	21.7	11/9/99	1/17/00	69
472	MW-68A	B	779679-0024	779679-0026	23.0	11/9/99	1/17/00	69
472	MW-68B	A	779679-0016	779679-0020	34.5	11/9/99	1/17/00	69
472	MW-68B	B	779679-0017	779679-0021	37.0	11/9/99	1/17/00	69
472	MW-68B	B repl	779679-0018	NA	37.0	11/9/99	1/17/00	69
472	MW-68B	C	779679-0019	779679-0022	38.5	11/9/99	1/17/00	69
472	MW-68C	A	779679-0027	779679-0050	56.0	11/9/99	1/17/00	69
472	MW-68C	B	779679-0028	779679-0051	57.5	11/9/99	1/17/00	69
472	MW-68C	C	779679-0117	779679-0116	59.0	11/9/99	1/19/00	71

Table 2. Sampler deployment and recovery information, Naval Air Station North Island, California, November 1999 to January 2000—Continued

[repl, replicate sample; NA, not applicable; *, low-flow bladder-pump sample; #, data from OHM Remediation Services Corporation (2000)]

Site or building designation	Well identifier	Sampling interval identifier	Low-flow sample laboratory identifier	Diffusion-sampler laboratory identifier	Depth to diffusion-sampler center (ft bls)	Date installed	Date recovered	Number of days diffusion samplers were in wells
472	MW-68C2	A	779679-0166	779679-0181	37.2	11/11/99	1/20/00	70
472	MW-68C2	B	779679-0169	779679-0182	39.1	11/11/99	1/20/00	70
472	MW-68C2	B repl	NA	779679-0183	39.1	11/11/99	1/20/00	70
472	MW-68C2	C	779679-0171	779679-0184	40.5	11/11/99	1/20/00	70
472	MW-68C2	D	779679-0173	779679-0185	42.0	11/11/99	1/20/00	70
472	MW-68C2	E	779679-0176	779679-0186	44.1	11/11/99	1/20/00	70
472	MW-68C2	F	779679-0178	779679-0187	46.0	11/11/99	1/20/00	70
472	MW-68C2	G	779679-0180	779679-0188	47.8	11/11/99	1/20/00	70
472	MW-68C2	H	779679-0179	779679-0189	49.8	11/11/99	1/20/00	70
472	MW-68C2	I	779679-0177	779679-0190	51.9	11/11/99	1/20/00	70
472	MW-68C2	J	779679-0174	779679-0191	53.9	11/11/99	1/20/00	70
472	MW-68C2	J repl	779679-0175	NA	53.9	11/11/99	1/20/00	70
472	MW-68C2	K	779679-0172	779679-0192	55.5	11/11/99	1/20/00	70
472	MW-68C2	L	779679-0170	779679-0193	57.5	11/11/99	1/20/00	70
472	MW-68C2	M	779679-0168	779679-0194	59.5	11/11/99	1/20/00	70
472	MW-68C2	M repl	NA	779679-0195	59.5	11/11/99	1/20/00	70
472	MW-68C2	N	779679-0167	779679-0196	61.5	11/11/99	1/20/00	70
379	PW-15	A	779679-0083	779679-0089	25.4	11/13/99	1/19/00	67
379	PW-15	B	779679-0084	779679-0118	27.1	11/13/99	1/19/00	67
379	PW-15	B repl	NA	779679-0119	27.1	11/13/99	1/19/00	67
379	PW-15	C	779679-0085	779679-0156	28.5	11/13/99	1/19/00	67
379	PW-15	D	779679-0086	779679-0157	30.2	11/13/99	1/19/00	67
379	PW-15	E	779679-0087	779679-0158	31.7	11/13/99	1/19/00	67
379	PW-15	E repl	NA	779679-0159	31.7	11/13/99	1/19/00	67
379	PW-15	F	779679-0088	779679-0164	33.1	11/13/99	1/19/00	67
379	PW-55	A	779679-0077	779679-0109	27.1	11/13/99	1/19/00	67
379	PW-55	B	779679-0078	779679-0110	28.9	11/13/99	1/19/00	67
379	PW-55	B repl	NA	779679-0114	28.9	11/13/99	1/19/00	67
379	PW-55	C	779679-0079	779679-0111	30.6	11/13/99	1/19/00	67
379	PW-55	D	779679-0080	779679-0112	31.9	11/13/99	1/19/00	67
379	PW-55	E	779679-0081	779679-0113	33.1	11/13/99	1/19/00	67
379	PW-55	E repl	779679-0082	779679-0115	33.1	11/13/99	1/19/00	67
379	PW-66	A	779679-0106	779679-0145	25.5	11/10/99	1/18/00	69
379	PW-66	B	779679-0107	779679-0146	27.3	11/10/99	1/18/00	69
379	PW-66	B repl	NA	779679-0151	27.3	11/10/99	1/18/00	69

Table 2. Sampler deployment and recovery information, Naval Air Station North Island, California, November 1999 to January 2000—Continued

[repl, replicate sample; NA, not applicable; *, low-flow bladder-pump sample; #, data from OHM Remediation Services Corporation (2000)]

Site or building designation	Well identifier	Sampling interval identifier	Low-flow sample laboratory identifier	Diffusion-sampler laboratory identifier	Depth to diffusion-sampler center (ft bls)	Date installed	Date recovered	Number of days diffusion samplers were in wells
379	PW-66	C	779679-0073	779679-0147	29.1	11/10/99	1/18/00	69
379	PW-66	D	779679-0108	779679-0148	30.8	11/10/99	1/18/00	69
379	PW-66	E	779679-0074	779679-0149	32.3	11/10/99	1/18/00	69
379	PW-66	F	779679-0075	779679-0150	33.9	11/10/99	1/18/00	69
379	PW-66	F repl	NA	779679-0152	33.9	11/10/99	1/18/00	69
Site 11	MW-12	A	779679-0006	779679-0012	30.5	11/13/99	1/17/00	65
Site 11	MW-12	B	779679-0007	779679-0013	32.1	11/13/99	1/17/00	65
Site 11	MW-12	C	779679-0008	779679-0014	33.7	11/13/99	1/17/00	65
Site 11	MW-12*	D	779679-0009	779679-0057	35.1	11/13/99	1/17/00	65
Site 11	MW-12*	D repl	NA	779679-0060	35.1	11/13/99	1/17/00	65
Site 11	MW-12	E	779679-0010	779679-0058	36.9	11/13/99	1/17/00	65
Site 11	MW-12	F	779679-0011	779679-0059	38.5	11/13/99	1/17/00	65
Site 11	MW-5D	A	779679-0121	779679-0128	50.8	11/12/99	1/18/00	67
Site 11	MW-5D	B	779679-0122	779679-0129	52.3	11/12/99	1/18/00	67
Site 11	MW-5D	C	779679-0123	779679-0130	54.2	11/12/99	1/18/00	67
Site 11	MW-5D	C repl	NA	779679-0134	54.2	11/12/99	1/18/00	67
Site 11	MW-5D*	D	779679-0124	779679-0131	55.75	11/12/99	1/18/00	67
Site 11	MW-5D	D repl	779679-0125	NA	55.75	11/12/99	1/18/00	67
Site 11	MW-5D	E	779679-0126	779679-0132	57.4	11/12/99	1/18/00	67
Site 11	MW-5D	F	779679-0127	779679-0133	59.0	11/12/99	1/18/00	67
Site 11	MW9*	NA	779679-0154	779679-0155	31	11/12/99	1/19/00	68
Site 2	S2-MW6A	A	779679-0062	779679-0135	6.5	11/13/99	1/18/00	66
Site 2	S2-MW6A	B	779679-0063	779679-0136	7.85	11/13/99	1/18/00	66
Site 2	S2-MW6A	C	779679-0064	779679-0137	9.2	11/13/99	1/18/00	66
Site 2	S2-MW6A	D	779679-0065	779679-0138	10.6	11/13/99	1/18/00	66
Site 2	S2-MW6A	E	779679-0066	779679-0139	11.95	11/13/99	1/18/00	66
Site 2	S2-MW6A	F	779679-0067	779679-0140	13.3	11/13/99	1/18/00	66
Site 2	S2-MW6A	G	779679-0068	779679-0141	14.65	11/13/99	1/18/00	66
Site 2	S2-MW6A	H	779679-0069	779679-0142	16.05	11/13/99	1/18/00	66
Site 2	S2-MW6A	I	779679-0070	779679-0143	17.5	11/13/99	1/18/00	66
Site 2	S2-MW6A	J	779679-0071	779679-0144	18.95	11/13/99	1/18/00	66
Site 2	S2-MW6A	J repl	779679-0072	NA	18.95	11/13/99	1/18/00	66

Table 3. Comparison of replicate samples collected by diffusion-sampler methodology, Naval Air Station North Island, California, January 2000

[repl, replicate sample; ft bls, feet below land surface; (µg/L, micrograms per liter; J, estimated value; U, value was below the analytical quantitation limit; 11DCA, 1,1-dichloroethane; 11DCE, 1,1-dichloroethene; cDCE, *cis*-1,2-dichloroethene; TCE, trichloroethene]

Well identifier and (depth code)	Depth to diffusion sampler center (ft bls)	Site or building designation	11DCA (µg/L)	11DCE (µg/L)	cDCE (µg/L)	Ethylbenzene (µg/L)	TCE (µg/L)	Vinyl chloride(µg/L)	Total xylenes (µg/L)
MW-12 (D)	35.1	Site 11	86 J	1,500	100	100 U	1,800	100 U	100 U
MW-12 (D-repl)	35.1	Site 11	89 J	1,500	110	100 U	1,700	100 U	100 U
MW-5D (C)	54.2	Site 11	170	2,800 E	61	50 U	930	50 U	50 U
MW-5D (C repl)	54.2	Site 11	170	2,900 E	61	50 U	930	50 U	50 U
MW-68C2 (B)	39.1	472	2,500 U	4,100	1,000 J	2,500 U	47,000	2,500 U	2,500 U
MW-68C2 (B repl)	39.1	472	5,000 U	4,300 J	960 J	5,000 U	52,000	5,000 U	5,000 U
MW-68C2 (M)	59.5	472	500 U	350 J	500 U	500 U	7,000	500 U	500 U
MW-68C2 (M repl)	59.5	472	500 U	360 J	500 U	500 U	6,800	500 U	500 U
PW-15 (B)	27.1	379	52	8	130	15	7	72	52
PW-15 (B repl)	27.1	379	54	8	130	17	5 J	75	57
PW-15 (E)	31.7	379	500 U	500 U	1,900	500 U	5,500	500 U	500 U
PW-15 (E repl)	31.7	379	500 U	500 U	1,900	500 U	5,600	500 U	500 U
PW-55 (B)	28.9	379	2,500 U	2,500 U	6,500	2,500 U	39,000	2,500 U	2,500 U
PW-55 (B repl)	28.9	379	2,500 U	2,500 U	6,700	2,500 U	36,000	2,500 U	2,500 U
PW-55 (E)	33.1	379	2,500 U	2,500 U	6,300	2,500 U	33,000	2,500 U	2,500 U
PW-55 (E repl)	33.1	379	2,500 U	2,500 U	6,100	2,500 U	31,000	2,500 U	2,500 U
PW-66 (B)	28.9	379	500 U	500 U	3,400	500 U	9,000	500 U	500 U
PW-66 (B repl)	28.9	379	500 U	500 U	3,200	500 U	9,200	500 U	500 U
PW-66 (F)	33.1	379	5 U	130	5 U	5 U	13	5 U	5 U
PW-66 (F repl)	33.1	379	5 U	120	5 U	5 U	18	5 U	5 U

obtained using the bladder pump (table 7). The reason for the difference in tetrachloroethene concentrations is not known.

The data from well MW-5 (site 11) show that the diffusion samplers performed favorably. At well MW-5, where a bladder pump was used to obtain water adjacent to a diffusion sampler and where peristaltic pumps were used at the other depths, the difference between the TCE concentration in water from the adjacent diffusion sampler and the average concentration (300 µg/L) in water from the bladder pump was relatively small (17-percent difference) (table 7). Moreover, the higher TCE concentration in water from the diffusion sampler compared to the concentration in water from the bladder pump implies that the sample collected by the diffusion method was more discrete than the sample collected by using the bladder pump.

A comparison between diffusion samples and a bladder pump sample at well MW-12 showed that the TCE concentration in water from the diffusion sampler was similar to the TCE concentration in water from the bladder pump (1,800 and 2,100 µg/L, respectively); however, the *cis*-1,2-dichloroethene (cDCE) concentration in water from the diffusion sampler was substantially lower (78 percent) than the concentration in water from the bladder pump (table 7 and fig. 2). This difference may be due to in-well mixing by low-flow sampling in a chemically stratified part of the screened interval. Data from diffusion samplers show that the VOC concentrations substantially increased with depth over a distance of only 3.4 ft and that the bladder pump was positioned at a transition zone between two depths of differing concentrations (table 5 and fig. 2). The bladder pump was sampled

Table 4. Comparison of replicate samples collected by low-flow methodology, Naval Air Station North Island, California, January 2000

[repl, replicate sample; *, sample collected by using bladder pump - low-flow samples without * were collected by using a peristaltic pump; #, data from OHM Remediation Services Corp. (2000); ft bls, feet below land surface; (µg/L, micrograms per liter; J, estimated value; U, value was below the analytical quantitation limit; 11DCA, 1,1-dichloroethane; 11DCE, 1,1-dichloroethene; cDCE, *cis*-1,2 dichloroethene; TCE, trichloroethene]

Well Identifier and (depth code)	Depth to diffusion sampler center (ft bls)	Site or building designation	11DCA (µg/L)	11DCE (µg/L)	cDCE (µg/L)	Ethylbenzene (µg/L)	TCE (µg/L)	Vinyl chloride (µg/L)	Total xylenes (µg/L)
MW-10 (G)	18.8	653	5 U	0 J	5 U	5 U	6	5 U	3 J
MW-10 (G repl)	18.8	653	5 U	5 U	1 J	5 U	9	5 U	5 U
MW-13B**	26	653	5 U	5 U	3,100	5 U	5 U	1,600	5 U
MW-13B** (repl)	26	653	5 U	5 U	3,200	5 U	5 U	1,400	5 U
MW-13C (B)	46.6	653	5 U	5 U	3 J	5 U	5 U	5 U	5 U
MW-13C (B repl)	46.6	653	5 U	5 U	2 J	5 U	5 U	5 U	5 U
MW-5D (D)*	55.7	Site 11	51	760	23 J	25 U	320	25 U	25 U
MW-5D (D repl)*	55.7	Site 11	44	670	22 J	25 U	280	25 U	25 U
MW-68C2 (J)	53.9	472	2,500 U	2,500 J	2,500 U	2,500 U	38,000	2,500 U	2,500 U
MW-68C2 (J repl)	53.9	472	2,500 U	2,600	2,500 U	2,500 U	38,000	2,500 U	2,500 U
MW-68B (B)	37.0	472	5,000 U	4,400 J	5,000 U	5,000 U	34,000	5,000 U	5,000 U
MW-68B (B repl)	37.0	472	5,000 U	4,900 J	5,000 U	5,000 U	33,000	5,000 U	5,000 U
PW-55 (E)	33.1	379	2,500 U	2,500 U	5,500	2,500 U	29,000	2,500 U	2,500 U
PW-55 (E repl)	33.1	379	2,500 U	2,500 U	5,700	2,500 U	29,000	2,500 U	2,500 U
S2-MW-6A (J)	18.9	Site 2	5 U	5 U	5 U	5 U	5 U	5 U	5 U
S2-MW-6A (J repl)	18.9	Site 2	5 U	5 U	5 U	5 U	5 U	5 U	5 U

following low-flow sampling from three overlying depths using a peristaltic pump; thus, the concentration interface potentially shifted upward toward the bladder pump intake. It is possible that in-well mixing was more pronounced for cDCE than for TCE because there was a greater percentage of change in concentrations with depth for cDCE than for TCE. The cDCE concentration increased by a factor of 26 (100 to 2,600 µg/L) over a depth of 3.4 feet, whereas TCE increased by only a factor of 4.6 over the same depth interval (1,700 to 7,800 µg/L) (fig. 2). The VOC concentration data indicate that in well MW-12, the diffusion samplers collected point samples of ground water, whereas the bladder pump either collected water from a greater radius of influence or from water induced up the well bore by low-flow sampling at shallower depths.

Wells MW-13A and MW-13B were tested using diffusion samplers and low-flow sampling with a peristaltic pump. Following sample collection with the peristaltic pump, the diffusion samplers were recovered and the wells were sampled by using a bladder pump (bladder-pump data from OHM Remediation Services Corporation, 2000). The data show that at well MW-13A, the cDCE and vinyl chloride concentrations in water obtained using the bladder pump were within the concentration ranges for water obtained from diffusion samplers that bracketed the depth interval of the bladder pump intake (table 7). At well MW-13B, the cDCE concentration also was within the range measured in those diffusion samplers bracketing the depth of the bladder pump intake (table 7 and fig. 3). Although vinyl chloride concentrations differed between the two methods by 16 to

Table 5. Concentrations of selected chlorinated volatile organic compounds in water from diffusion and low-flow sampling, Naval Air Station North Island, California, January 2000

[µg/L, micrograms per liter; D, sample was diluted; U, value was below the analytical quantitation limit; J, estimated value; NA, not applicable; E, the detected result is between the sample-specific estimated quantitation and the method detection limit; *, sample collected by using bladder pump; #, data from OHM Remediation Services Corporation (2000)]

Well	Depth (feet)	1,1-Dichloroethane (µg/L)		1,1-Dichloroethene (µg/L)		<i>cis</i> -1,2-Dichloroethene (µg/L)		Tetrachloroethene (µg/L)		Trichloroethene (µg/L)		Vinyl chloride (µg/L)	
		Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow
MW-5D	50.8	260	200	1,500	1,900 D	66	62	50 U	25 U	690	660	50 U	25 U
MW-5D	52.3	260	210	3,600	4,300 D	120 J	63	250 U	50 U	1,200	1,100	250 U	50 U
MW-5D	54.2	170	95 J	3,200 D	1,400	61	36 J	50 U	100 U	930	590	50 U	100 U
MW-5D*	55.8	65	51	1,500 D	760	27	23 J	5 U	25 U	510 D	320	5 U	25 U
MW-5D	57.4	50 U	20	460	360 D	50 U	11	50 U	5 U	160	120	50 U	5 U
MW-5D	59.0	50 U	6	190	94	10 J	6	50 U	5 U	55	36	50 U	5 U
MW-9*	27.6	270	270	4,000	3,500	250 U	250 U	260	330	3,300	3,200	250 U	250 U
MW-10	7.8	5 U	5 U	5 U	2 J	5 U	5 U	5 U	5 U	5 U	30	5 U	5 U
MW-10	9.2	5 U	5 U	5 U	1 J	5 U	5 U	5 U	5 U	5 U	18	5 U	5 U
MW-10	11.2	5 U	5 U	5 U	1 J	1 J	5 U	5 U	5 U	5 U	17	5 U	5 U
MW-10	13.2	5 U	5 U	5 U	1 J	5 U	5 U	5 U	5 U	5 U	13	5 U	5 U
MW-10	15.2	5 U	5 U	5 U	0 J	5 U	5 U	5 U	5 U	5 U	10	5 U	5 U
MW-10	17.2	5 U	5 U	5 U	0 J	5 U	5 U	5 U	5 U	5 U	9	5 U	5 U
MW-10	18.9	5 U	5 U	5 U	0 J	5 U	5 U	5 U	5 U	5 U	6	5 U	5 U
MW-12	30.5	94 J	73	1,500	970 D	99 J	77	100 U	4 J	1,700	1,400 D	100 U	5 U
MW-12	32.2	91 J	52	1,500	510 D	96 J	57	100 U	2 J	1,700	800 D	100 U	5 U
MW-12	33.7	91 J	87	1,500	780 D	93 J	140	100 U	2 J	1,900	960 D	100 U	5 U
MW-12*	35.1	86 J	260	1,500	2,200	100	450	100 U	100 U	1,800	2,100	100 U	100 U
MW-12	37.0	230	890	2,600	3,700	500	1,500	100 U	500 U	2,400	3,800	100 U	500 U
MW-12	38.5	1,600	1,800	8,800	7,900	2,600	3,000	500 U	500 U	7,800	7,600	500 U	500 U

Table 5. Concentrations of selected chlorinated volatile organic compounds in water from diffusion and low-flow sampling, Naval Air Station North Island, California, January 2000—Continued

[µg/L, micrograms per liter; D, sample was diluted; U, value was below the analytical quantitation limit; J, estimated value; NA, not applicable; E, the detected result is between the sample-specific estimated quantitation and the method detection limit; *, sample collected by using bladder pump; #, data from OHM Remediation Services Corporation (2000)]

Well	Depth (feet)	1,1-Dichloroethane (µg/L)		1,1-dichloroethene (µg/L)		Cis-1,2-dichloroethene (µg/L)		Tetrachloroethene (µg/L)		Trichloroethene (µg/L)		Vinyl chloride (µg/L)	
		Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow
MW-13A	6.5	5 U	5 U	5 U	5 U	39	47	5 U	5 U	5 U	5 U	4 J	6
MW-13A	8.0	5 U	5 U	5 U	5 U	78	46	5 U	5 U	5 U	5 U	9	6
MW-13A	9.4	5 U	5 U	5 U	5 U	77	47	5 U	5 U	5 U	5 U	9	6
MW-13A	10.9	5 U	5 U	5 U	5 U	74	53	5 U	5 U	5 U	5 U	8	7
MW-13A	12.4	5 U	5 U	5 U	5 U	46	55	5 U	5 U	5 U	5 U	5	7
MW-13A*#	12.0	NA	5 U	NA	5 U		61	NA	5 U	NA	5 U	NA	7
MW-13B	24.9	5 U	5 U	4 J	4 J	3,100 D	2,600 D	5 U	5 U	4 J	5	1,900 D	1,900 D
MW-13B	26.2	5 U	5 U	4 J	5 U	2,600 D	2,600 D	5 U	5 U	4 J	6	2,000 D	1,600 D
MW-13B	27.6	5 U	5 U	5 J	5 J	2,700 D	2,900 D	5 U	5 U	8	7	2,400 D	1,700 D
MW-13B*#	26.0	NA	5 U	NA	5 U	NA	3,100	NA	5 U	NA	5 U	NA	1,400
MW-13C	45.5	5 U	5 U	5 U	5 U		2 J	5 U	5 U	5 U	5 U	5 U	5 U
MW-13C	46.7	5 U	5 U	5 U	5 U	5 U	3 J	5 U	5 U	5 U	5 U	5 U	5 U
MW-13C	48.1	5 U	5 U	5 U	5 U	5 U	2 J	5 U	5 U	5 U	5 U	5 U	5 U
MW-13C*#	46.0	NA	5 U	NA	5 U	NA	1 J	NA	5 U	NA	5 U	NA	5 U
MW-68A	21.7	7 J	4 J	25 U	5 U	140	81	7 J	2 J	570	320 D	25 U	5 U
MW-68A	23.0	50 U	5 J	50 U	5 U	160	87	50 U	1 J	730	190	50 U	5 U
MW-68B	34.5	85 J	5,000 U	5,800	4,700 J	87 J	5,000 U	93 J	5,000 U	49,000 D	28,000	250 U	5,000 U
MW-68B	37.0	5,000 U	5,000 U	7,700	4,400 J	5,000 U	5,000 U	5,000 U	5,000 U	62,000	34,000	5,000 U	5,000 U
MW-68B	38.5	5,000 U	5,000 U	8,300	5,000 J	5,000 U	5,000 U	5,000 U	5,000 U	130,000	62,000	5,000 U	5,000 U
MW-68C	56.0	50 U	50 U	20 J	50 U	50 U	50 U	50 U	50 U	1,400	680	50 U	50 U
MW-68C	57.5	100 U	50 U	100 U	10 J	100 U	50 U	100 U	50 U	2,700	880	100 U	50 U
MW-68C	59.0	250 U	50 U	250 U	50 U	250 U	50 U	250 U	50 U	4,100	1,100	250 U	50 U

Table 5. Concentrations of selected chlorinated volatile organic compounds in water from diffusion and low-flow sampling, Naval Air Station North Island, California, January 2000—Continued

[µg/L, micrograms per liter; D, sample was diluted; U, value was below the analytical quantitation limit; J, estimated value; NA, not applicable; E, the detected result is between the sample-specific estimated quantitation and the method detection limit; *, sample collected by using bladder pump; #, data from OHM Remediation Services Corporation (2000)]

Well	Depth (feet)	1,1-Dichloroethane (µg/L)		1,1-Dichloroethene (µg/L)		<i>cis</i> -1,2-Dichloroethene (µg/L)		Tetrachloroethene (µg/L)		Trichloroethene (µg/L)		Vinyl chloride (µg/L)	
		Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow
MW-68C2	37.3	1,000 U	500 U	2,400	1,200	490 J	360 J	1,000 U	500 U	19,000	9,100	1,000 U	500 U
MW-68C2	39.1	2,500 U	2,500 U	4,100	3,400	1,000 J	2,500 U	2,500 U	2,500 U	47,000	34,000	2,500 U	2,500 U
MW-68C2	40.5	5,000 U	2,500 U	5,400	2,700	5,000 U	2,500 U	5,000 U	2,500 U	84,000	39,000	5,000 U	2,500 U
MW-68C2	42.1	10,000 U	2,500 U	14,000	2,800	10,000 U	2,500 U	10,000 U	2,500 U	200,000	46,000	10,000 U	2,500 U
MW-68C2	44.2	10,000 U	2,500 U	7,800 J	3,600	10,000 U	2,500 U	10,000 U	2,500 U	110,000	54,000	10,000 U	2,500 U
MW-68C2	46.1	10,000 U	1,000 U	7,500 J	1,200	10,000 U	1,000 U	10,000 U	1,000 U	110,000	17,000	10,000 U	1,000 U
MW-68C2	47.9	10,000 U	5,000 U	7,400 J	4,300 J	10,000 U	5,000 U	10,000 U	5,000 U	110,000	55,000	10,000 U	5,000 U
MW-68C2	49.9	10,000 U	2,500 U	7,200 J	4,400	10,000 U	2,500 U	10,000 U	2,500 U	100,000	53,000	10,000 U	2,500 U
MW-68C2	52.0	2,500 U	2,500 U	3,000	2,800	2,500 U	2,500 U	2,500 U	2,500 U	42,000	42,000	2,500 U	2,500 U
MW-68C2	53.9	1,000 U	2,500 U	1,100	2,500 J	1,000 U	2,500 U	1,000 U	2,500 U	14,000	38,000	1,000 U	2,500 U
MW-68C2	55.6	500 U	1,000 U	600	1,000	500 U	1,000 U	500 U	1,000 U	8,800	14,000	500 U	1,000 U
MW-68C2	57.5	500 U	500 U	450 J	710	500 U	500 U	500 U	500 U	7,300	9,100	500 U	500 U
MW-68C2	59.5	500 U	500 U	350 J	920	500 U	500 U	500 U	500 U	7,000	11,000	500 U	500 U
MW-68C2	61.5	500 U	500 U	280 J	740	500 U	500 U	500 U	500 U	6,500	11,000	500 U	500 U
PW-15	25.4	45	53	4 J	12	42	200 E	5 U	2 J	4 J	15	82	66
PW-15	27.1	52	52	5	22	130	850 D	1 J	8	7	92	72	29
PW-15	28.5	73 J	77 J	36 J	66 J	1,500	2,200	100 J	250 U	180	2,500	100 U	250 U
PW-15	30.2	97 J	500 U	250 U	500 U	2,900	1,600	59 J	500 U	3,000	4,700	250 U	500 U
PW-15	31.8	500 U	500 U	500 U	500 U	1,900	1,800	500 U	500 U	5,500	5,800	500 U	500 U
PW-15	33.2	500 U	500 U	500 U	500 U	2,400	2,100	120 J	130 J	7,500	7,300	500 U	500 U
PW-55	27.1	2,500 U	2,500 U	2,500 U	2,500 U	7,300	5,700	2,500 U	2,500 U	39,000	31,000	2,500 U	2,500 U
PW-55	28.9	2,500 U	2,500 U	2,500 U	2,500 U	6,500	5,900	2,500 U	2,500 U	39,000	32,000	2,500 U	2,500 U
PW-55	30.6	2,500 U	2,500 U	2,500 U	2,500 U	6,600	5,900	2,500 U	2,500 U	38,000	34,000	2,500 U	2,500 U

Table 5. Concentrations of selected chlorinated volatile organic compounds in water from diffusion and low-flow sampling, Naval Air Station North Island, California, January 2000—Continued

[µg/L, micrograms per liter; D, sample was diluted; U, value was below the analytical quantitation limit; J, estimated value; NA, not applicable; E, the detected result is between the sample-specific estimated quantitation and the method detection limit; *, sample collected by using bladder pump; #, data from OHM Remediation Services Corporation (2000)]

Well	Depth (feet)	1,1-Dichloroethane (µg/L)		1,1-Dichloroethene (µg/L)		<i>cis</i> -1,2-Dichloroethene (µg/L)		Tetrachloroethene (µg/L)		Trichloroethene (µg/L)		Vinyl chloride (µg/L)	
		Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow
PW-55	31.9	2,500 U	2,500 U	2,500 U	2,500 U	6,800	5,300	2,500 U	2,500 U	38,000	29,000	2,500 U	2,500 U
PW-55	33.1	2,500 U	2,500 U	2,500 U	2,500 U	6,300	5,500	2,500 U	2,500 U	33,000	29,000	2,500 U	2,500 U
PW-66	25.5	1,000 U	500 U	1,000 U	38 J	2,000	1,600	1,000 U	599 U	17,000	13,000	1,000 U	500 U
PW-66	27.3	500 U	500 U	500 U	500 U	3,400	1,000	500 U	500 U	9,000	6,400	500 U	500 U
PW-66	29.1	50 U	500 U	38 J	500 U	23 J	500 U	50 U	500 U	770	9,800	50 U	500 U
PW-66	30.8	25 U	500 U	49	500 U	25 U	500 U	25 U	500 U	180	5,600	25 U	500 U
PW-66	32.3	5 U	500 U	72	500 U	5 U	500 U	5 U	500 U	48	6,200	5 U	500 U
PW-66	33.9	5 U	500 U	130	500 U	5 U	500 U	1 J	500 U	13	6,000	5 U	500 U
S2-MW-6A	6.5	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
S2-MW-6A	7.9	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	2 U	5 U	5 U
S2-MW-6A	9.2	5 U	5 U	5 U	5 U	5 U	5						
S2-MW-6A	10.6	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	2 J	2 J	5 U	5 U
S2-MW-6A	12.0	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	2 J	5 U	5 U
S2-MW-6A	13.3	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	1 J	5 U	5 U	5 U
S2-MW-6A	14.7	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	2 J	5 U	5 U
S2-MW-6A	16.1	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	2 J	5 U	5 U
S2-MW-6A	17.5	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	2 J	5 U	5 U
S2-MW-6A	19.0	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U

Table 6. Concentrations of benzene, ethylbenzene, toluene, and total xylenes in water from diffusion and low-flow sampling, Naval Air Station North Island, California, January 2000

[µg/L, micrograms per liter; U, value was below the analytical quantitation limit; J, estimated value; NA, not applicable; *, sample collected by using bladder pump; #, data from OHM Remediation Services Corporation (2000)]

Well	Depth (feet)	Benzene (µg/L)		Ethylbenzene (µg/L)		Toluene (µg/L)		Total xylenes (µg/L)	
		Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow
MW-5D	50.8	50 U	25 U	50 U	25 U	50 U	25 U	50 U	25 U
MW-5D	52.3	250 U	50 U	250 U	50 U	250 U	50 U	250 U	50 U
MW-5D	54.2	50 U	100 U	50 U	100 U	50 U	100 U	50 U	100 U
MW-5D*	55.8	5 U	25 U	5 U	25 U	5 U	25 U	5 U	25 U
MW-5D	57.4	50 U	5 U	50 U	5 U	50 U	5 U	50 U	5 U
MW-5D	59.0	50 U	5 U	50 U	5 U	50 U	5 U	50 U	5 U
MW-9*	27.6	250 U	250 U	250 U	250 U	250 U	250 U	250 U	250 U
MW-10	7.8	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
MW-10	9.2	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
MW-10	11.2	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
MW-10	13.2	5 U	5 U	5 U	5 U	5 U	5 U	1 J	5 U
MW-10	15.2	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
MW-10	17.2	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
MW-10	18.9	5 U	5 U	5 U	5 U	5 U	5 U	5 U	25 J
MW-12	30.5	100 U	5 U	100 U	5 U	100 U	5 U	100 U	5 U
MW-12	32.2	100 U	5 U	100 U	5 U	100 U	5 U	100 U	5 U
MW-12	33.7	100 U	5 U	100 U	5 U	100 U	5 U	100 U	5 U
MW-12*	35.1	100 U	100 U	100 U	100 U	100 U	100 U	100 U	100 U
MW-12	37.0	100 U	500 U	100 U	120 U	100 U	500 U	100 U	360 U
MW-12	38.5	500 U	500 U	500 U	500 U	500 U	500 U	500 U	500 U
MW-13A	6.5	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
MW-13A	8.0	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
MW-13A	9.4	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
MW-13A	10.9	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
MW-13A	12.4	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
MW-13A*#	12.0	NA	5 U	NA	5 U	NA	5 U	NA	
MW-13B	24.9	9	5	5 U	5 U	5 U	5 U	5 U	5 U
MW-13B	26.2	5	4 J	5 U	5 U	5 U	5 U	5 U	5 U
MW-13B	27.6	1 J	4 J	5 U	5 U	1 J	5 U	5 U	5 U
MW13B*#	26.0	NA	5 U	NA	5 U	NA	5 U	NA	5 U
MW-13C	45.5	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
MW-13C	46.7	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U

Table 6. Concentrations of benzene, ethylbenzene, toluene, and total xylenes in water from diffusion and low-flow sampling, Naval Air Station North Island, California, January 2000—Continued

[µg/L, micrograms per liter; U, value was below the analytical quantitation limit; J, estimated value; NA, not applicable; *, sample collected by using bladder pump; #, data from OHM Remediation Services Corporation (2000)]

Well	Depth (feet)	Benzene (µg/L)		Ethylbenzene (µg/L)		Toluene (µg/L)		Total xylenes (µg/L)	
		Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow
MW-13C	48.1	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
MW-13C*#	46.0	NA	5 U	NA	5 U	NA	5 U	NA	5 U
MW-68A	21.7	25 U	5 U	25 U	5 U	25 U	5 U	25 U	5 U
MW-68A	23.0	50 U	5 U	50 U	5 U	50 U	5 U	50 U	5 U
MW-68B	34.5	250 U	5,000 U	250 U	5,000 U	250 U	5,000 U	250 U	5,000 U
MW-68B	37.0	5,000 U	5,000 U	5,000 U	5,000 U	5,000 U	5,000 U	5,000 U	5,000 U
MW-68B	38.5	5,000 U	5,000 U	5,000 U	5,000 U	5,000 U	5,000 U	5,000 U	5,000 U
MW-68C	56.0	50 U	50 U	50 U	50 U	50 U	50 U	50 U	50 U
MW-68C	57.5	100 U	50 U	100 U	50 U	100 U	50 U	100 U	50 U
MW-68C	59.0	250 U	12 J	250 U	50 U	250 U	50 U	250 U	50 U
MW-68C2	37.3	1,000 U	500 U	1,000 U	500 U	1,000 U	500 U	1,000 U	500 U
MW-68C2	39.1	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U
MW-68C2	40.5	5,000 U	2,500 U	5,000 U	2,500 U	5,000 U	2,500 U	5,000 U	2,500 U
MW-68C2	42.1	10,000 U	2,500 U	10,000 U	2,500 U	10,000 U	2,500 U	10,000 U	2,500 U
MW-68C2	44.2	10,000 U	2,500 U	10,000 U	2,500 U	10,000 U	2,500 U	10,000 U	2,500 U
MW-68C2	46.1	10,000 U	1,000 U	10,000 U	1,000 U	10,000 U	1,000 U	10,000 U	1,000 U
MW-68C2	47.9	10,000 U	5,000 U	10,000 U	5,000 U	10,000 U	5,000 U	10,000 U	5,000 U
MW-68C2	49.9	10,000 U	2,500 U	10,000 U	2,500 U	10,000 U	2,500 U	10,000 U	2,500 U
MW-68C2	52.0	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U
MW-68C2	53.9	1,000 U	2,500 U	1,000 U	2,500 U	1,000 U	2,500 U	1,000 U	2,500 U
MW-68C2	55.6	500 U	1,000 U	500 U	1,000 U	500 U	1,000 U	500 U	1,000 U
MW-68C2	57.5	500 U	500 U	500 U	500 U	500 U	500 U	500 U	500 U
MW-68C2	59.5	500 U	500 U	500 U	500 U	500 U	500 U	500 U	500 U
MW-68C2	61.5	500 U	500 U	500 U	500 U	500 U	500 U	500 U	500 U
PW-15	25.4	4 J	2 J	16	9	7	3 J	75	28
PW-15	27.1	3 J	3 J	15	3 J	5 J	5 U	52	7
PW-15	28.5	100 U	250 U	100 U	250 U	100 U	250 U	100 U	250 U
PW-15	30.2	250 U	500 U	250 U	500 U	250 U	500 U	250 U	500 U
PW-15	31.8	500 U	500 U	500 U	500 U	500 U	500 U	500 U	500 U
PW-15	33.2	500 U	500 U	500 U	500 U	500 U	500 U	500 U	500 U
PW-55	27.1	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U
PW-55	28.9	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U
PW-55	30.6	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U

Table 6. Concentrations of benzene, ethylbenzene, toluene, and total xylenes in water from diffusion and low-flow sampling, Naval Air Station North Island, California, January 2000—Continued

[µg/L, micrograms per liter; U, value was below the analytical quantitation limit; J, estimated value; NA, not applicable; *, sample collected by using bladder pump; #, data from OHM Remediation Services Corporation (2000)]

Well	Depth (feet)	Benzene (µg/L)		Ethylbenzene (µg/L)		Toluene (µg/L)		Total xylenes (µg/L)	
		Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow	Diffusion	Low flow
PW-55	31.9	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U
PW-55	33.1	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U	2,500 U
PW-66	25.5	1,000 U	500 U	1,000 U	500 U	1,000 U	500 U	1,000 U	500 U
PW-66	27.3	500 U	500 U	500 U	500 U	500 U	500 U	500 U	500 U
PW-66	29.1	50 U	500 U	50 U	500 U	50 U	500 U	50 U	500 U
PW-66	30.8	25 U	500 U	25 U	500 U	25 U	500 U	25 U	500 U
PW-66	32.3	5 U	500 U	5 U	500 U	5 U	500 U	5 U	500 U
PW-66	33.9	5 U	500 U	5 U	500 U	5 U	500 U	5 U	500 U
S2-MW-6A	6.5	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
S2-MW-6A	7.9	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
S2-MW-6A	9.2	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
S2-MW-6A	10.6	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
S2-MW-6A	12.0	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
S2-MW-6A	13.3	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
S2-MW-6A	14.7	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
S2-MW-6A	16.1	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
S2-MW-6A	17.5	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
S2-MW-6A	19.0	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U

20 percent, the concentrations obtained using the diffusion samplers were slightly higher than those concentrations obtained using the bladder pump. The concentrations obtained using the diffusion samplers in well MW-13B were slightly higher, but similar to the concentrations obtained using the peristaltic pump (fig. 3). Concentrations of toluene and total xylenes were present in water obtained from both the diffusion samplers and the peristaltic pump (fig. 3); toluene and total xylenes were not detectable (less than 5 µg/L) in water from the bladder pump. The data suggest that the diffusion samplers performed equally well with the bladder pump in wells MW-13A and MW-13B for cDCE. The higher concentrations of vinyl chloride, toluene, and total xylenes in water from the diffusion samplers relative to water from the bladder pump indicate that the diffusion samplers obtained more discrete samples from these wells; however, disturbing the well water by using the peristaltic pump and removing the

diffusion samplers prior to sampling with the bladder pump may have induced mixing and affected the quality of the water sampled by the bladder pump.

Comparison of Diffusion-Sampler Results to Peristaltic-Pump Results

The remaining comparisons between diffusion-sampler and low-flow sampler methods utilized multiple diffusion-sampling and low-flow sampling points within screened intervals. At most depths, low-flow sampling was conducted by using peristaltic pumps. In contrast to bladder pumps, using peristaltic pumps in some wells potentially could cause degassing of samples during recovery, which could result in underestimating actual VOC concentrations. Thus, VOC concentrations in water obtained using peristaltic

Table 7. Comparison of concentrations of selected volatile organic compounds in water from a diffusion sampler and in water from low-flow purging using a bladder pump at the same depth, Naval Air Station North Island, California, January 2000

[*, average percent difference; -, concentration measured in diffusion sampler was lower than concentration measured in low-flow sample]

Constituent	Diffusion samples		Low-flow bladder-pump samples		Percent difference
	Depth, in feet below land surface	Concentration, in micrograms per liter	Depth, in feet below land surface	Concentration, in micrograms per liter	
Well MW-9					
1,1-Dichloroethene (1,1-DCE)	31	4,000	31	3,500	2.0
Tetrachloroethene (PCE)	31	260	31	330	-21.0
Trichloroethene (TCE)	31	3,300	31	3,200	3.0
Well MW-5					
Trichloroethene (TCE)	55.75	360	55.75	280, 320	17*
Well MW-12					
cis-1,2-Dichloroethene (cDCE)	35.1	100	35.1	450	-78
Trichloroethene (TCE)	35.1	1,800	35.1	2,100	-14
Well MW-13A					
cis-1,2-Dichloroethene (cDCE)	10.9 - 12.4	46 - 74	12	61	Within range
Vinyl chloride	10.9 - 12.4	5 - 8	12	7.4	Within range
Well MW-13B					
cis-1,2-Dichloroethene (cDCE)	24.85 - 26.15	3,100 - 2,600	26	3,100	Within range
Toluene	24.85 - 26.15	9	26	<5	Not applicable
Total xylenes	24.85 - 26.15	111 - 110	26	<5	Not applicable
Vinyl chloride	24.85 - 26.15	1,900 - 2,000	26	1,600	18*

pumps may be representative of concentrations in ground water at some wells but may underestimate actual concentrations in ground water at other wells. Moreover, when multiple depths within a screened interval are purged using low-flow methods, there is a potential for each low-flow sampling event to disturb the equilibrated water column. If the pumping rate during low-flow sampling is low enough to prevent drawdown in the well, then all of the pumped water is replaced by ground water from the aquifer; however, the zone of influence contributing water to the well may not be adjacent to the pump. Thus, in a chemically stratified screened interval where multiple depth intervals are sequentially sampled, water entering the well screen from early low-flow samplings may influence concentrations obtained in later samplings as a result of vertical transport and mixing in the well screen. Despite these uncertainties, the use of multiple-level low-flow sampling methods using

peristaltic pumps sometimes can provide an estimate of contaminant vertical distribution in the screened interval, which can be used as a comparison for the diffusion samplers.

In most of the observation wells, the vertical concentration gradients obtained using the diffusion-sampler and low-flow sampler methods were similar. However, in several cases, the concentrations in water obtained by using the peristaltic pump were lower than the concentrations in water obtained by using the diffusion samplers (figs. 4, 5, and 6). An example of this is TCE concentrations measured in water from wells MW-68A, MW-68B, and MW-68C. TCE concentrations were approximately 43 to 73 percent lower in water samples collected by using low-flow sampling methods and peristaltic pumps than in samples collected by the diffusion samplers. This substantial difference in concentrations between the two methods is expected if VOCs were lost by degassing as a result of

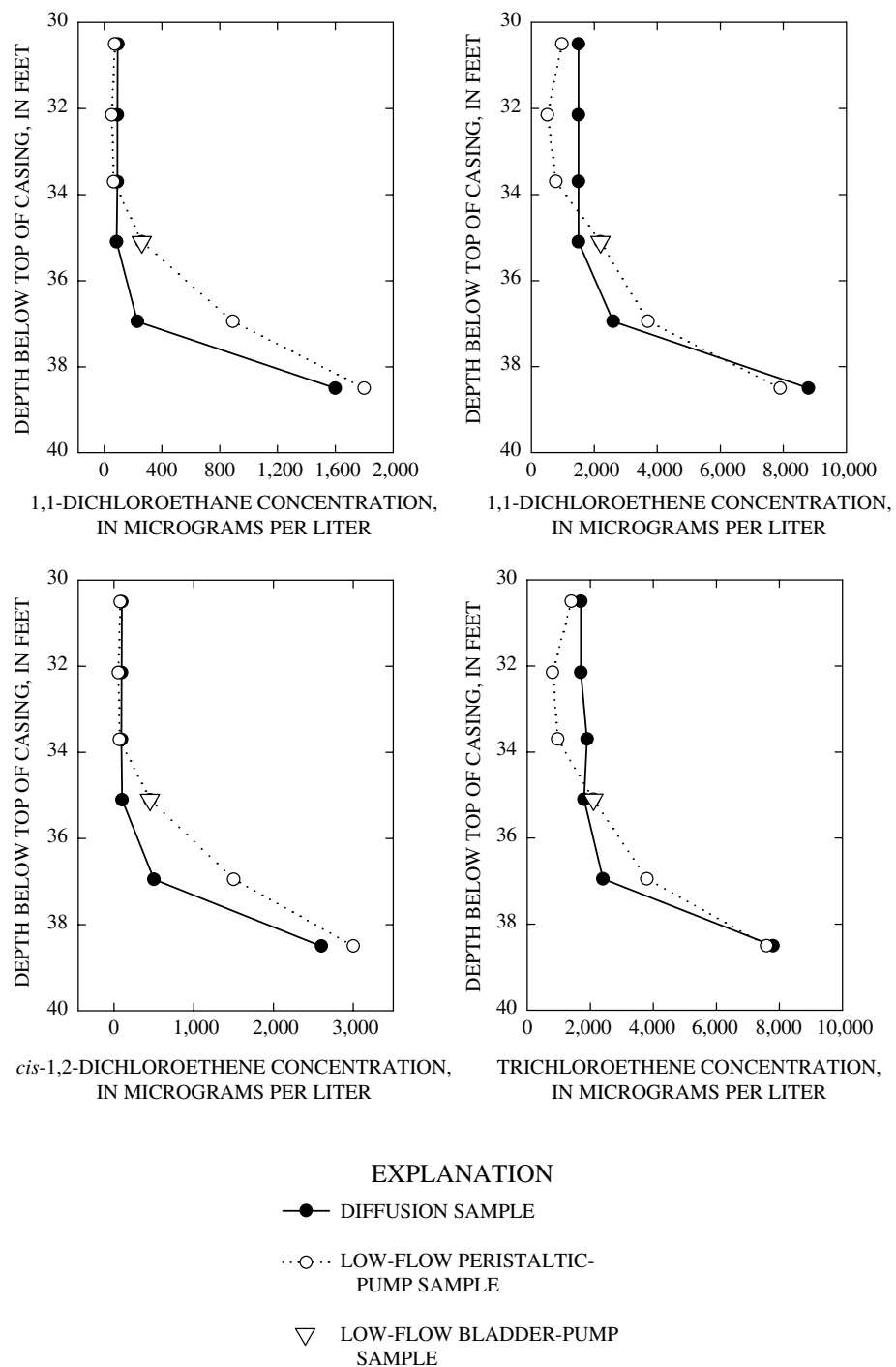


Figure 2. Comparison of diffusion and low-flow samples in ground water at well MW-12, Naval Air Station North Island, California, January 2000.

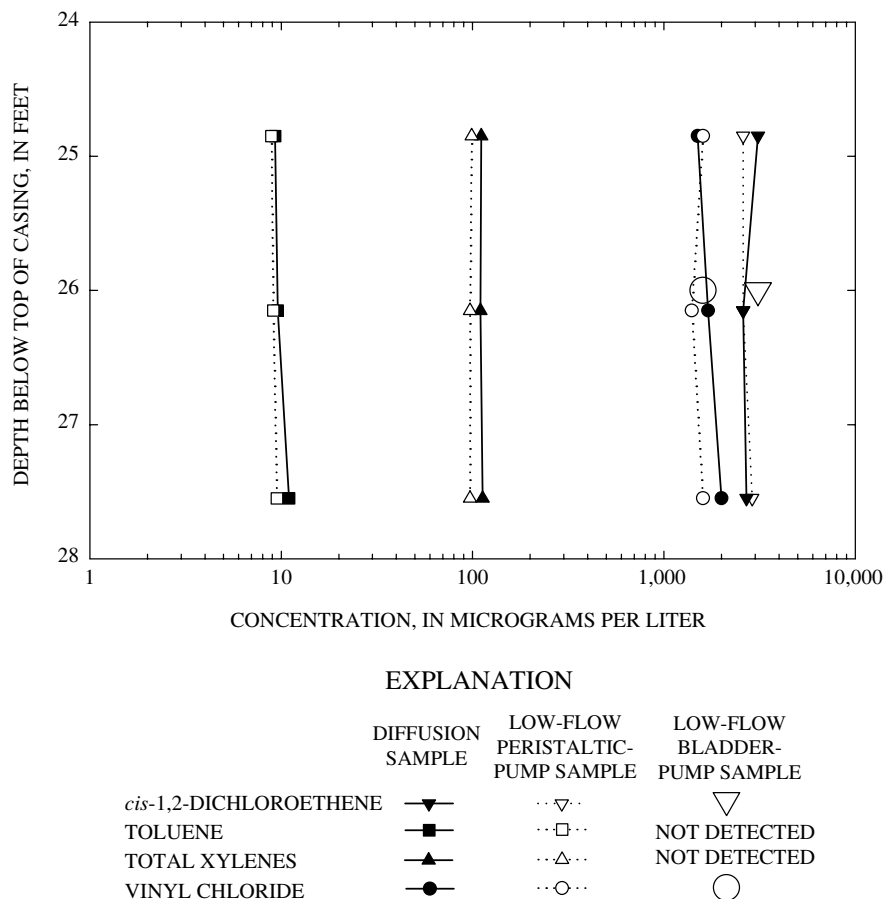


Figure 3. Comparison of diffusion and low-flow samples in ground water at well MW-13B, Naval Air Station North Island, California, January 2000.

using peristaltic pumps or if mixing in the well screens occurred during pumping. The vertical concentration distribution between the two methods implies that the VOC concentrations measured in water from diffusion samplers reflected the vertical distribution of contaminants in the aquifer adjacent to the screened interval more accurately than the peristaltic-pump sampling.

Further comparison of TCE concentration data from the two sampling methods indicates that diffusion sampling provides a point sample, whereas sequential low-flow sampling of multiple horizons within a single well screen can induce mixing. In general, the vertical sequence of low-flow sampling in the wells began with the shallowest depth interval and ended with the deepest interval. In well PW-66, TCE data show that concentrations in water collected with a diffusion sampler were highest in the shallowest sampled depth, and then decreased sharply over the 5-ft depth interval below this shallowest depth (fig. 7).

Although the highest TCE concentration obtained by low-flow sampling also was at the shallowest horizon, it was approximately 24 percent lower than the concentration obtained from the corresponding diffusion sampler, and the vertical stratification was less sharply defined. These data suggest that as low-flow sampling with a peristaltic pump progressed vertically downward, the pumping gradually mixed the TCE-contaminated water from the shallowest sampling depth with water from deeper intervals, thus obscuring the original contaminant stratification (fig. 7).

A similar effect can be seen in the data from wells MW-12 and PW-15 (figs. 2 and 8). At these wells, the shallowest interval was relatively uncontaminated. The comparison between diffusion samples and low-flow samples at this shallowest depth showed a relatively close match between *c*DCE and TCE concentrations. However, as sampling progressed vertically downward toward the interface of the

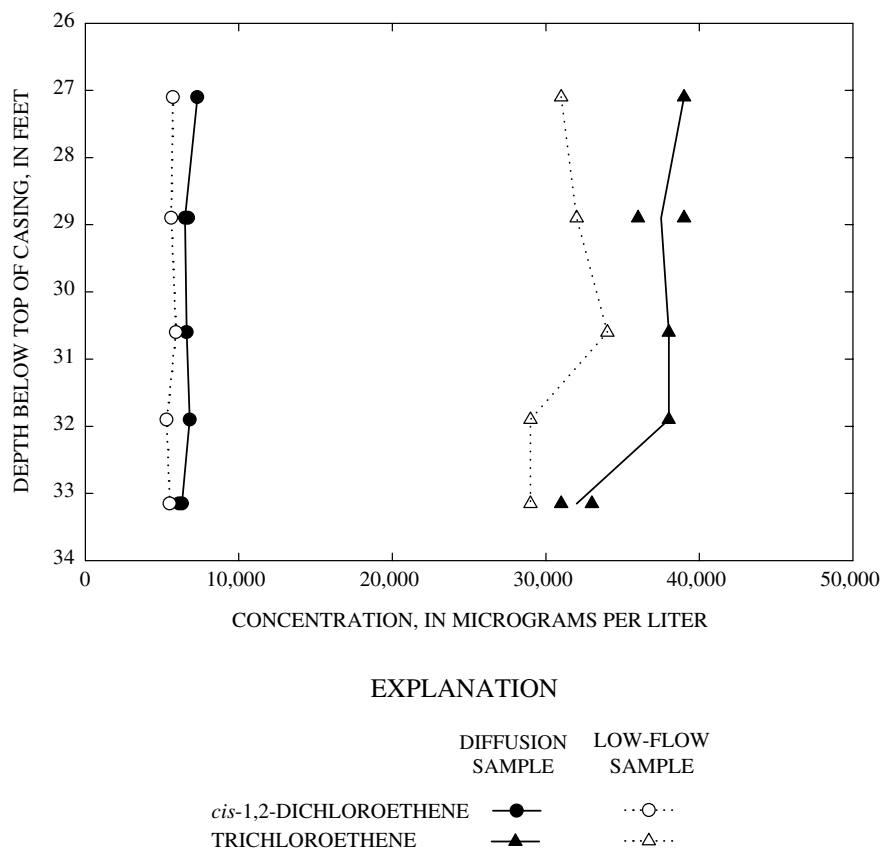


Figure 4. Comparison of diffusion and low-flow samples in ground water at well PW-55, Naval Air Station North Island, California, January 2000.

stratified contamination, the low-flow sample concentrations generally increased higher than the diffusion-sample concentrations, which is to be expected if the zone of influence for the low-flow pumping captured the more contaminated ground water in the well. In general, the data suggest that diffusion sampling provides a more precise delineation of the contaminant stratification within the screened interval than low-flow sampling.

Insight into the use of diffusion samplers in a chemically stratified screened interval can be observed in the data from wells at the MW-68 cluster (figs. 6D and 6E). Unlike the other wells, two peristaltic pumps were used to low-flow sample well MW-68C2. Starting simultaneously from both the uppermost and the lowermost sample depths, sampling progressed sequentially toward the center of the 25-ft screened interval. Results from both the diffusion samples and the low-flow samples showed that the uppermost and lowermost parts of the screened interval were relatively uncontaminated. Concentration data from the

diffusion samples show that substantially higher TCE concentrations occurred between depths of approximately 40 to 50 ft, with a sharp peak at about 42 ft (fig. 6D). Thus, the first water pulled into the well screen from both ends of the screen was relatively uncontaminated. As the low-flow sampling progressed toward the center of the screened interval, the correlation between concentrations obtained from the diffusion samples began to differ substantially from those obtained by low-flow sampling (fig. 6D). Between the depths of approximately 40 to 50 ft, TCE concentrations from low-flow sampling were approximately 47 to 84 percent lower than TCE concentrations from diffusion samplers; additionally, the low-flow sampling data did not indicate a TCE peak concentration at a depth of 42 ft as shown by the diffusion sampling data. A probable explanation for the concentration differences between the two methods is that initially, relatively uncontaminated water was pumped into the screened interval, thus mixing the ground water in the well and diluting concentrations of TCE. As a result,

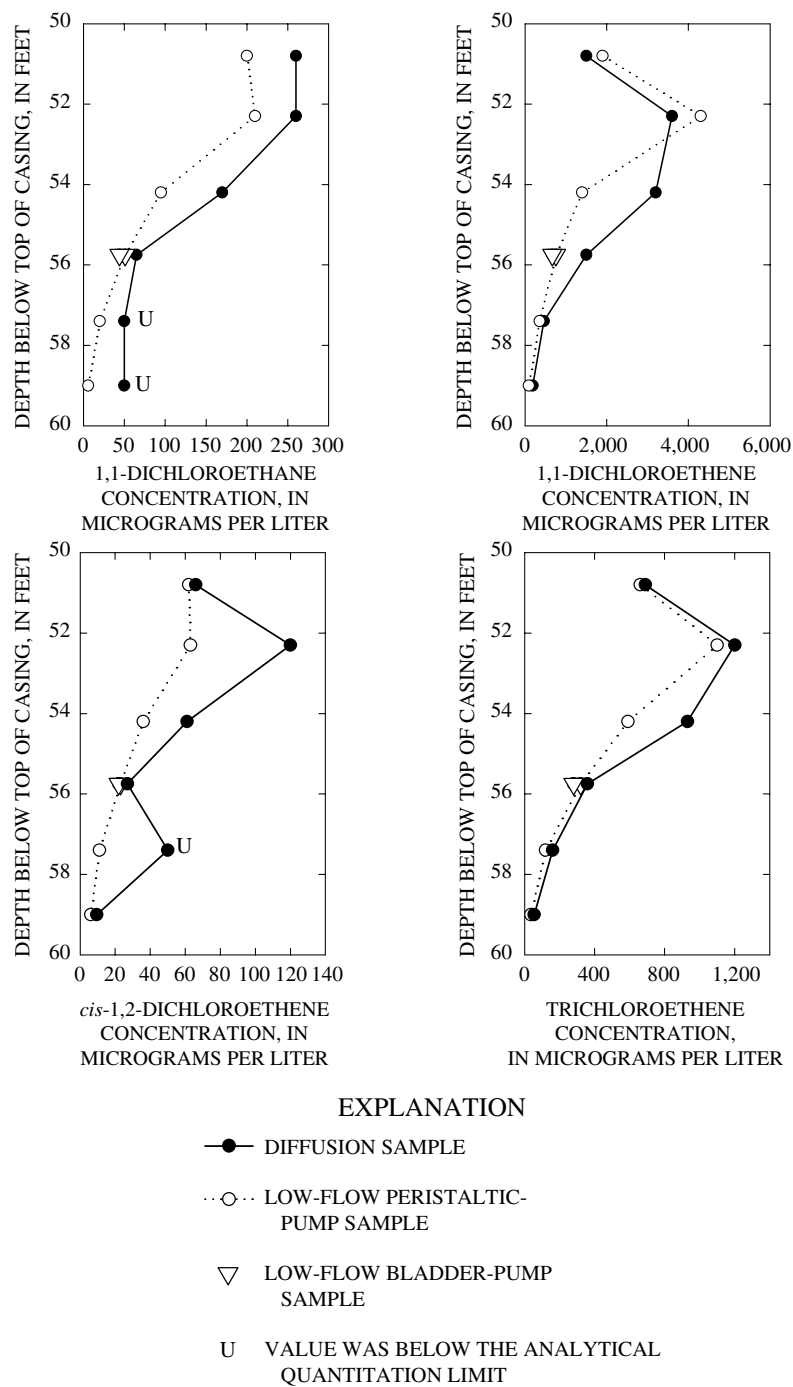


Figure 5. Comparison of diffusion and low-flow samples in ground water at well MW-5, Naval Air Station North Island, California, January 2000.

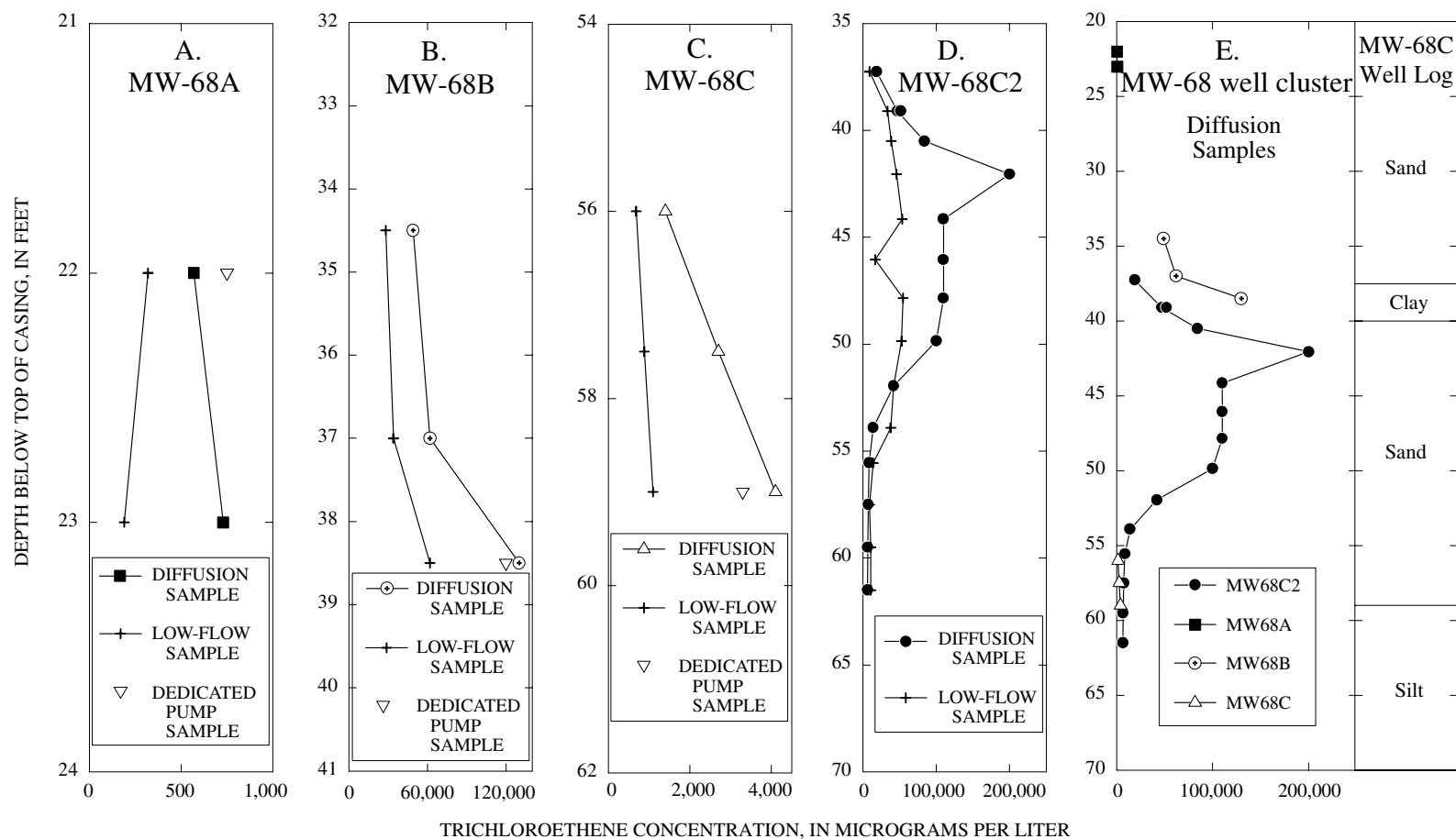


Figure 6. Comparison of diffusion and low-flow samples in ground water at wells (A) MW-68A, (B) MW-68B, (C) MW-68C, and (D) MW-68C2, and (E) comparison of diffusion samples from multiple wells to geologic log of well MW-68C, Naval Air Station North Island, California, January 2000.

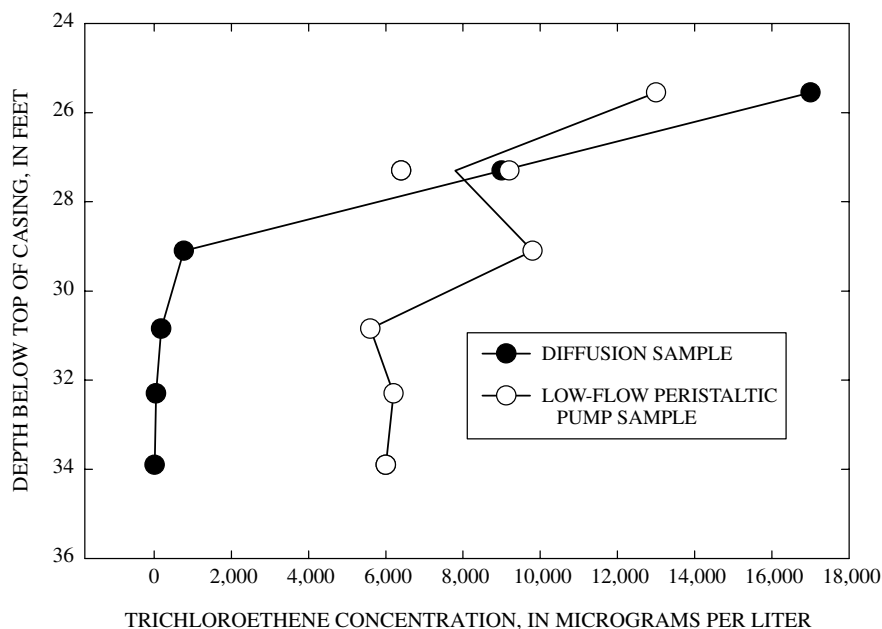


Figure 7. Comparison of trichloroethene concentrations in diffusion and low-flow samples in ground water at well PW-66, Naval Air Station North Island, California 2000.

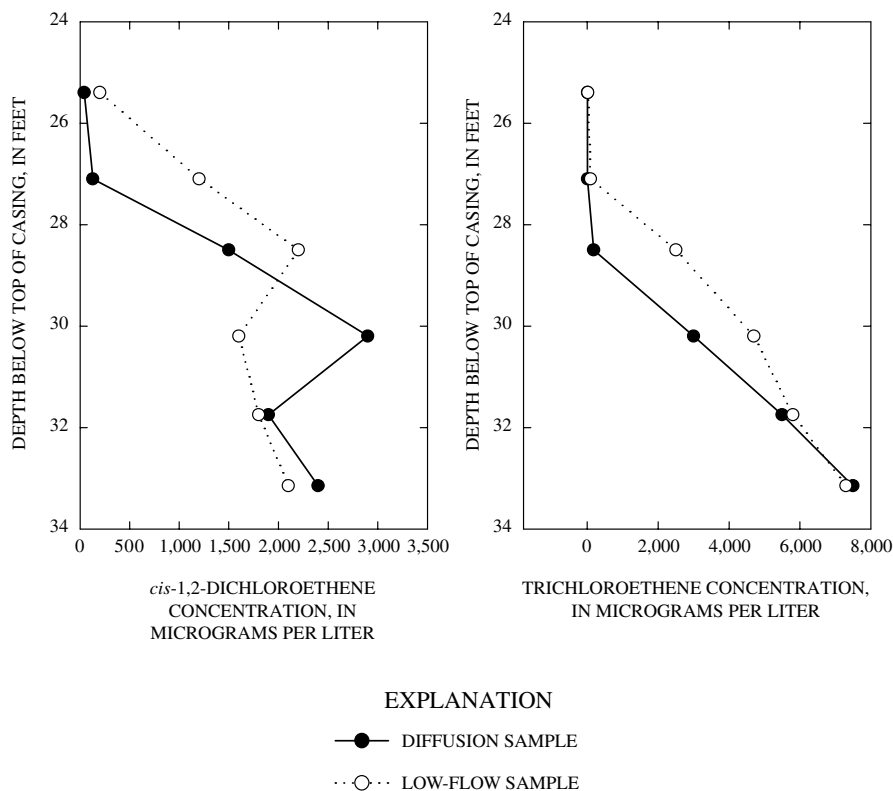


Figure 8. Comparison of diffusion and low-flow samples in ground water at well PW-15, Naval Air Station North Island, California, January 2000.

TCE concentrations were lowered in ground water collected from subsequently sampled depths. Additional VOC losses by degassing during the use of peristaltic pumps probably resulted in further concentration differences between the two sampling methods.

TCE concentration data in diffusion samplers collected from wells MW-68B and MW-68C and concentration data in diffusion samplers collected from adjacent well MW-68C2 support the vertical distribution indicated by the diffusion samplers in well MW-68C2 (figs. 6B, 6C, and 6D). Diffusion samplers from well MW-68C2 indicate that the lowest concentrations in the screened interval are below a depth of approximately 55 ft, and the detected concentrations are similar to those from the same depth in the adjacent well MW-68C (fig. 6E).

Similarly, diffusion samplers from wells MW-68C2 and MW-68B both indicate TCE concentrations increasing with depth between approximately 35 and 40 ft (fig. 6E). The TCE concentrations in diffusion samples from well MW-68B are higher than those from the corresponding depth in well MW-68C2 (fig. 6E). The reasons for the concentration difference between wells MW-68C2 and MW-68B are not known; however, two explanations can be postulated. One explanation is that the contaminant concentrations in well MW-68C2 may have been shifted downward as a result of a vertical hydraulic gradient within the well. Water-level measurements are not shown for well MW-68C2 because they would reflect only compositing across the screened interval; however, evidence for such a hydraulic gradient can be seen in the water-level data for wells MW-68B and MW-68C. The water level in well MW-68B is 0.34 ft higher than the water level in well MW-68C, indicating a net downward hydraulic gradient between the two depths (table 1). Water levels remeasured in March 2000 confirmed the hydraulic gradient. Because well MW-68C2 is only about 5 ft from wells MW-68B and MW-68C, and because the screened interval of well MW-68C2 hydraulically connects the depths sampled by wells MW-68B and MW-68C, the probability is high that there also is a downward hydraulic gradient within well MW-68C2. An alternative explanation is that lithologic heterogeneities in the screened zone place the contamination at slightly different depths in different wells. Evidence for such heterogeneity is the clay layer at a depth of 37.5 to 40 ft in well MW-68C (driller's log, Richard Wong, OHM Remediation, written commun., 2000). Despite the uncertainty regarding

concentration differences between wells, the diffusion samplers appear to have been successful in approximately locating the zone of highest concentrations between the depths of 37 to 52 ft (fig. 6E).

VOC concentrations in water collected from well MW-13A varied less and generally were lower for peristaltic pump sampling compared to diffusion sampling (fig. 9). Following low-flow sampling using a peristaltic pump, well MW-13A was immediately resampled by low-flow sampling using a bladder pump. Although subject to the same mixing potential as the peristaltic pump, the bladder pump has less potential for volatilization loss than the peristaltic pump, and thus, probably provides a more representative sample than the peristaltic pump. The concentrations of cDCE and TCE in water obtained using low-flow sampling methods with a bladder pump approximated the average of concentrations obtained in water from the diffusion samplers directly above and below the bladder pump (fig. 8). These findings suggest that data obtained by using the diffusion samplers provided depth-specific VOC concentrations while the data from low-flow sampling represented a mixing of waters in well MW-13A.

In well MW-10, low-flow peristaltic-pump sampling detected low concentrations (30 µg/L or less) of TCE, whereas diffusion sampling detected none (table 5). This difference in concentrations is unusual because the potential for volatilization loss using the peristaltic pump usually results in underestimating ambient concentrations, while diffusion samplers are capable of producing representative samples even at low (less than 20 µg/L) concentrations. According to historical data (OHM Remediation Services Corporation, 2000), TCE has never previously been detected in well MW-10 (sampling dates July 1998, March 1999, June 1999, and September 1999). Furthermore, a resampling of the well using low-flow methodology at multiple horizons in February 2000 also showed that TCE was not present. Thus, it seems that the diffusion samplers accurately reflected VOC concentrations in ground water; the source of low TCE concentrations found in water obtained from low-flow, peristaltic-pump sampling is unknown, but may represent a cross-contamination source not related to local ground water.

Wells S2-MW-06A and MW-13C contained no detectable VOCs (less than 5 µg/L) in water from either the diffusion samples or from the low-flow samples. Thus, the construction materials used in the

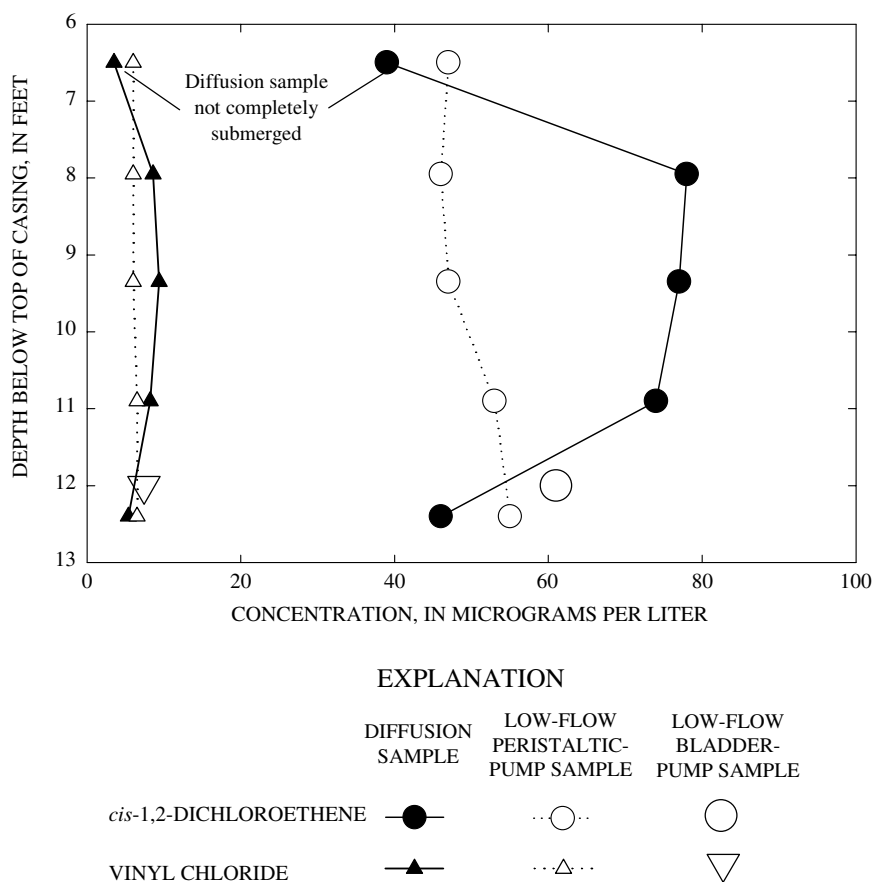


Figure 9. Comparison of diffusion and low-flow samples in ground water well MW-13A, Naval Air Station North Island California, January 2000.

diffusion samplers did not contribute contaminants to the water.

the free-phase fuel in ground water from well MW-11 also contained TCE (table 5).

Diffusion Samplers in Free-Phase Fuel

The diffusion samplers deployed in buckets containing free-phase JP-5 and Stoddard solution from wells MW-11 and PW-17 did not show evidence of structural integrity loss during the 2 months of equilibration. The VOCs detected in the free-phase fuel also were detected in the water from the diffusion samplers (table 8). The VOC concentrations in water from the diffusion samplers were lower than the VOC concentrations in the fuel; however, this is to be expected because the first is an aqueous solution and the second is an organic solvent concentration. The diffusion samplers provided an alternative method for showing that

Contaminant Stratification in Well Screens

The data from this investigation show that substantial stratification of VOCs can be present within a 10-ft well screen. At four observation wells (MW-12, MW-5, PW-66, and PW-15), the data showed a sharp layering of VOCs within the screened interval (figs. 2, 5, 7, and 8). The diffusion-sampler data show that the vertical change in TCE concentrations over a distance of about 5 ft was approximately 17,500 µg/L in well PW-66, approximately 7,300 µg/L in well PW-15, and approximately 5,900 µg/L in well MW-12. At well MW-5, the 1,1-DCE concentration changed by 3,410 µg/L, and the TCE concentration changed by

Table 8. Concentrations of selected volatile organic compounds in free-phase jet fuel (JP-5) removed from ground water and in water from diffusion samplers deployed in a bucket containing the free-phase fuel, Naval Air Station North Island, California, January 2000

[µg/L, micrograms per liter; J, estimated value; U, value was below the analytical quantitation limit]

Sample source	1,1-Dichloroethane (µg/L)		1,1-Dichloroethene (µg/L)		cis-1,2-Dichloroethene (µg/L)		Tetrachloroethene (µg/L)		Trichloroethene (µg/L)	
	Diffusion sampler water	Free-phase fuel	Diffusion sampler water	Free-phase fuel	Diffusion sampler water	Free-phase fuel	Diffusion sampler water	Free-phase fuel	Diffusion sampler water	Free-phase fuel
Free product from well PW-17	4 J	5,000 U	5 U	5,000 U	3.9 J	5,000 U	5 U	5,000 U	2 J	5,000 U
Free product from well MW-11	10 U	5,000 U	10 U	5,000 U	10 U	5,000 U	7 J	4,300 J	65	5,200
	Vinyl chloride (µg/L)		Benzene (µg/L)		Ethylbenzene (µg/L)		Toluene (µg/L)		Total xylenes (µg/L)	
	Diffusion sampler water	Free-phase fuel	Diffusion sampler water	Free-phase fuel	Diffusion sampler water	Free-phase fuel	Diffusion sampler water	Free-phase fuel	Diffusion sampler water	Free-phase fuel
Free product from well PW-17	5 U	5,000 U		5,000 U	70	21,000	112	1,100 J	350	100,000
Free product from well MW-11	10 U	5,000 U	10 U	5,000 U	13	5,700	10 U	5,000 U	120	43,000

1,145 µg/L over a vertical distance of about 7 ft (fig. 5). The concentrations decreased with depth at some wells [MW-5 and PW-66 (figs. 5 and 7, respectively)] and increased with depth at others [MW-12 and PW-15 (figs. 2 and 8, respectively)].

The presence of contaminant stratification in well screens has importance for ground-water sampling. In an environment with a sharp concentration gradient, small disturbances in the water column can obscure the stratification. Thus, small amounts of mixing during low-flow sampling can result in large variations in VOC concentrations from pumped samples.

In addition, the potential for stratification is an important consideration when selecting a sampling depth. For example, the data indicate that if the dedicated bladder pump at well MW-12 had been set about 3 ft deeper, the pump would have been in contact with water containing approximately 6,000 µg/L more TCE than was present at the original sampling depth. If the dedicated bladder pump at well MW-5 had been set about 3 ft shallower, the pump would have been in contact with water containing approximately 690 µg/L higher concentrations of TCE. This consideration is even more important for diffusion samplers, which sample only the water in the immediate vicinity of the sampler. Therefore, when using diffusion samplers in a well where chemical stratification is suspected within the screened interval, multiple diffusion samplers can

be used to at least initially delineate the stratification. Analytical costs during such an investigation can be minimized by using field gas chromatography to delineate the stratification and to select particular samples for more detailed laboratory analyses.

SUMMARY

The ground-water VOC concentrations obtained by using water-filled polyethylene diffusion samplers were compared to the ground-water VOC concentrations obtained by using low-flow sampling methods with a peristaltic pump and dedicated bladder pumps in observation wells at Naval Air Station North Island, California. Comparisons of VOC concentrations obtained by using bladder pumps and diffusion samplers showed a generally good correlation. Concentrations of 1,1-dichloroethene (1,1-DCE) and trichloroethene (TCE) in ground water obtained from well MW-9 obtained using the diffusion sampler agreed well (12 and 3 percent difference, respectively) with those samples obtained using the bladder pump. At well MW-5, the TCE concentration in water from the diffusion sampler was higher than in water from the bladder pump, implying that the sample collected by the bladder pump may have underestimated actual concentrations as a result of mixing. Similarly, the

higher concentrations of vinyl chloride, toluene, and total xylenes in water from the diffusion samplers in wells MW-13A and MW-13B compared to water from the bladder pump imply that the concentrations obtained by the bladder pump may have underestimated actual concentration as a result of mixing in these wells. Concentration differences between the diffusion sampling and bladder-pump sampling methods were noted in samples from well MW-12, and probably are related to mixing in a chemically stratified part of the screened interval. The findings of this investigation suggest that diffusion samplers provide a viable sampling alternative for VOCs in ground water in most tested wells at NAS North Island.

Comparisons of volatile organic compound (VOC) concentrations in water obtained by using diffusion samplers to concentrations obtained by low-flow sampling using a peristaltic pump were used to gain information on the vertical distribution of contamination in the wells. In several wells, the probable effects of mixing or volatilization during pumping resulted in lower VOC concentrations in water obtained by using the peristaltic pump compared to concentrations obtained by using the diffusion samplers; however, the data from the low-flow sampling supported the vertical VOC stratification identified by using the diffusion samplers.

Substantial VOC stratification was observed in the screened intervals of several observation wells (MW-12, MW-5, PW-15, and PW-66). The diffusion-sampler data show that the vertical change in TCE concentrations over a distance of about 5 ft was approximately 17,500 µg/L in well PW-66, approximately 7,300 µg/L in well PW-15, and approximately 5,900 µg/L in well MW-12. At well MW-5, the 1,1-DCE concentration changed by 3,410 µg/L, and the TCE concentration changed by 1,145 µg/L over a vertical distance of about 7 ft. Concentrations decreased with depth at some wells (PW-66 and MW-5) and increased with depth at others (MW-12 and PW-15). The presence of stratification in well screens is important for ground-water sampling because small disturbances in the water column can mix the stratification, resulting in large variations in VOC concentrations from pumped samples. The data imply that care must be exercised when selecting a sampling depth. When using diffusion samplers in a well where chemical stratification is suspected within the screened interval, multiple diffusion samplers can be used to at least initially delineate the stratification.

Analytical costs during such an investigation can be minimized by using field gas chromatography or indicator-tube technology to delineate the stratification and to select particular samples for more detailed laboratory analyses.

The diffusion samplers deployed in buckets containing free-phase JP-5 and Stoddard solution collected from observation wells did not show evidence of structural integrity loss during the 2 months of equilibration. The VOCs detected in the free-phase fuel also were detected in water from the diffusion samplers.

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Investigation of Polyethylene Passive Diffusion Samplers for Sampling
Volatile Organic Compounds in Ground Water at Davis Global
Communication, Sacramento, California,
August 1998 to February 1999
USGS Open-File Report 00-307

By Don A. Vroblesky, James W. Borchers, Ted R. Campbell, and Willey Kinsey

Investigation of Polyethylene Passive Diffusion Samplers for Sampling Volatile Organic Compounds in Ground Water at Davis Global Communications, Sacramento, California, August 1998 to February 1999

By Don A. Vroblesky¹, James W. Borchers², Ted R. Campbell¹, and Willey Kinsey²

ABSTRACT

Fourteen wells were instrumented with diffusion samplers as a test to determine whether the samplers could be used to obtain representative volatile organic compound concentrations at a study site in Sacramento, California. Single diffusion samplers were placed in 10-foot-long well screens, and multiple diffusion samplers were positioned in 20-foot-long well screens. Borehole geophysical logs and electromagnetic flowmeter tests were run in selected wells with 20-foot-long well screens prior to deploying the samplers. The diffusion samplers were recovered after 25 to 30 days, and the wells were then sampled by using the purge-and-sample method. In most wells, the concentrations obtained by using the downhole diffusion samplers closely matched those obtained by using the purge-and-sample method. In seven wells, the concentrations differed between the two methods by only 2 micrograms per liter ($\mu\text{g/L}$) or less. In three wells, volatile organic compounds were not detected in water obtained by using either method. In the four remaining wells, differences

between the methods were less than 2 $\mu\text{g/L}$ in the 0.2- to 8.5- $\mu\text{g/L}$ concentration range and from 1.2 to 8.7 $\mu\text{g/L}$ in the 10- to 26- $\mu\text{g/L}$ concentration range. Greater differences (23 percent or 14.5 $\mu\text{g/L}$, 31 percent or 66 $\mu\text{g/L}$, and 46 percent or 30 $\mu\text{g/L}$) between the two methods were observed for tetrachloroethene concentrations, which ranged between 30 and 211 $\mu\text{g/L}$ in three wells. The most probable explanation for the differences is that in some wells, the purging induced drawdowns and introduced water that differed in volatile organic compound concentrations from the in situ water in contact with the screened interval of the well. Alternate explanations include the possibility of unrecorded changes in nearby contaminant-extraction-well operation during the equilibration period. The data suggest that the combined use of borehole flowmeter tests and diffusion samplers may be useful in optimizing the radius of capture of contaminated ground water by the contaminant-removal wells. Overall, the data suggest that the use of diffusion samplers provided an alternative sampling method to the purge-and-sample approach.

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INTRODUCTION

The U.S. Geological Survey (USGS), in cooperation with the U.S. Air Force Center for Environmental Excellence (AFCEE), began an initiative in August 1998 to investigate the suitability of using polyethylene water-filled passive diffusion samplers to collect volatile organic compound (VOC) samples from observation wells at Davis Global Communications in Sacramento, California. Passive diffusion samplers have been successfully used to obtain representative water samples for VOC concentrations without the need to purge at a different site (Vroblesky and Hyde, 1997). Thus, the diffusion samplers offer a potential savings in sampling time and expense relative to the purge-and-sample approach. The purpose of this report is to present results comparing VOC concentrations in water obtained from diffusion samplers to concentrations in water obtained by using the purge-and-sample approach.

Site Description

Davis Global Communications (fig. 1) is an annex of McClellan Air Force Base (AFB) in Sacramento, Calif., approximately 4 miles south of the city of Davis. The site, which has been in operation since the 1950's, is used for military communications. In 1985, three underground storage tanks were found to be leaking diesel fuel. During the course of the field investigation for hydrocarbon contamination, the presence of chlorinated solvents also was detected in the ground water. The source of the chlorinated solvents is unknown.

The geology of the site consists of fine-grained flood plain or overbank deposits mixed with lesser amounts of sandy stream deposits containing discontinuous gravels and sands. Driller's logs of the wells indicate that some of the silty and silty clay layers are fractured (CH2M HILL, 1994), possibly providing conduits for the vertical movement of ground water. Hydraulic testing to determine aquifer properties has not been done; however, most of the wells sampled for this investigation yielded little water and recovered slowly, strongly suggesting that the sampled horizons have a relatively low hydraulic conductivity.

Ground-water levels and flow directions at the site vary seasonally because of the influence of nearby agricultural wells, which typically are from 200- to 500-feet (ft) deep. Ground-water levels are

approximately 40 ft below mean sea level (msl) during the growing season when the agricultural wells are actively pumped; water levels rise about 40 ft during the winter when the wells are not used (CH2M HILL, 1994). In addition, onsite contaminant-removal wells are in operation most of the time, resulting in localized flow toward these pumped wells.

Methods

Fourteen wells at the site were instrumented with diffusion samplers during December 15–18, 1998. Of these wells, eight were equipped with screen lengths of 20 ft and six had screen lengths of 10 ft (table 1). In the wells having 10-ft-long screens, a single diffusion sampler was centered vertically in the screened interval. In wells having 20-ft-long screens, 9 or 10 diffusion samplers were placed end-to-end along a vertical profile within the screened interval.

Prior to installing the diffusion samplers, six of the 20-ft-long screened intervals were investigated by using borehole geophysical and flowmeter logging techniques. Logging was performed during the same week that the samplers were deployed (December 15–18, 1998). The depths of the wells and water levels were measured prior to installing the logging equipment. The wells then were logged using an electromagnetic induction and gamma tool and a fluid resistivity and temperature tool. An electromagnetic flowmeter was used under static and pumped conditions to measure vertical flow rates at discrete locations within the screened interval. At each tested well, a submersible pump was placed directly above the screened interval; fluid-resistivity and temperature logs were run, and vertical-flow measurements were made while the well was pumped.

The diffusion samplers were allowed to equilibrate within the screened interval for approximately 25 to 30 days. The samplers were recovered by removing them from the well, cutting open the polyethylene, and gently pouring the contents into 40-milliliter (mL) glass sampling vials with Teflon caps.

Immediately following diffusion-sampler recovery, the wells were purged and sampled in accordance with the ongoing ground-water protocol at the site. Well purging consisted of removing three casing volumes of water using a Grundfos submersible positive-displacement pump. Water samples then were collected from the well by using a bailer.

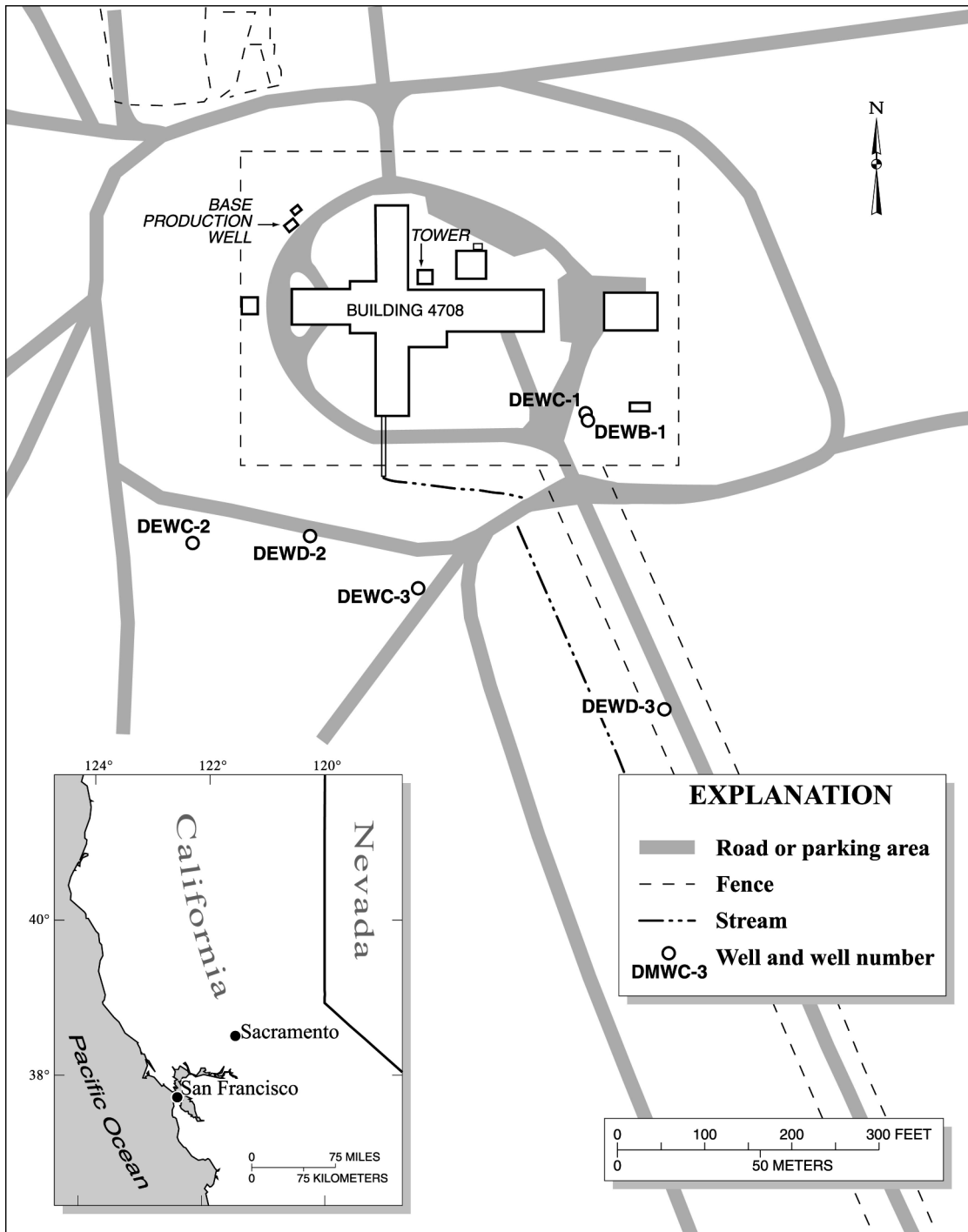


Figure 1. Locations of wells at Davis Global Communications, Sacramento, Calif., January 1999 (modified from Radian International, 1999).

Table 1. Construction data and number of installed diffusion samplers for tested wells at Davis Global Communications, Sacramento, Calif.

[ft, feet; msl, mean sea level; bls, below land surface; in., inches]

Well	Top of casing elevation (ft msl)	Ground-surface elevation (ft msl)	Screened interval (ft bls)	Casing diameter (in.)	Screen length (ft)	Total well depth (ft)	Number of diffusion samplers recovered
DMW-2	26.88	28.1	61–81	4	20	84	9
DMW-3	28.82	29.86	61–81	4	20	83.5	9
DMW-5	26.47	26.88	59–79	4	20	84	9
DMW-6	25.94	25.26	59–79	4	20	80.5	10
DMW-7	27.02	27.5	61–81	4	20	84	10
DMW-8	26.88	26.5	60–80	4	20	84	10
DMWD-3	28.68	27.06	155–175	4	20	250	10
DMWD-14	28.57	26.33	149–169	5	20	178	10
DMWC-3	29.16	26.94	93–103	4	10	108	1
DMWC-4	27.57	24.64	95–105	4	10	106	1
DMWD-10	29.22	27.02	162–172	5	10	173	1
DMWD-1	31.9	30.2	152–162	4	10	240	1
DMWD-11	29.29	27.42	171–181	5	10	181.5	1
DPC-22	28.11	Not measured	91–101	4	10	104	1

All samples were stored on ice and shipped to the same laboratory for analysis by using the U.S. Environmental Protection Agency (USEPA) Method 8260b. For 20-ft-long screened wells containing multiple diffusion samplers, only one of the diffusion samplers was sent to a USEPA-certified laboratory for analysis by USEPA Method 8260b. To select the representative sample for each 20-ft-long screened well, the sampling vials for each diffusion sampler were stored on ice and sent by overnight mail to the USGS in South Carolina.

Upon arrival at the USGS, an extra vial from each diffusion sampler was analyzed by head-space gas chromatography using a Photovac 10S Plus gas chromatograph. The remaining vials for the diffusion sampler containing the highest VOC concentrations at each well were stored on ice and sent by overnight mail

to the same USEPA-certified laboratory that analyzed the water collected by using the purge-and-sample method. The samples were analyzed by USEPA Method 8260b. The laboratory analytical results for the diffusion samplers were used as a standard for the concentrations obtained using head-space analysis in the respective well. Thus, in the graphs showing vertical concentration differences, the concentrations at one depth (designated in table 2) at each well represents the USEPA Method 8260b analysis of diffusion-sampler water. The remaining samples at that well represent USGS head-space gas chromatography analyses adjusted relative to the head-space analysis of the sampler analyzed by USEPA Method 8260b. Only the samples analyzed by USEPA Method 8260b were used directly to compare the two sampling methods in this investigation.

Table 2. Analytical results from ground-water samples obtained by using diffusion samplers and using the purge-and-sample method, Davis Global Communications, Calif., January 1999

[ft, feet; TCE, trichloroethene; PCE, tetrachloroethene; *c*DCE, *cis*-1,2-dichloroethene; 1,1-DCE, 1,1-dichloroethene; µg/L, micrograms per liter; Dif, water-filled diffusion sampler; P&S, purge-and-sample; J, analyte concentration considered an estimated value because one or more quality control specifications were not met; < less than]

Location	Sample type	Date sampled	Sample depth (ft)	TCE (µg/L)	PCE (µg/L)	<i>c</i> DCE (µg/L)	1,1-DCE (µg/L)
20-foot-long well screens							
DMW-2	Dif	1/13/99	67–68	17.3	1.7	4.5	0.8 J
	P&S	1/14/99	61–81	26.0 J	3.5	5.4	.7 J
DMW-3	DIF	1/13/99	71–72	10.7	47.2	.3 J	3.6
	P&S	1/14/99	61–81	10.7	61.7	.3 J	2.5
DMW-5	DIF	1/13/99	69–70	19.8	145.0	.3 J	10.5
	P&S	1/14/99	59–79	23.8	211.0	.2 J	8.8
DMW-6	DIF	1/14/99	61–62	19.7	35.3	1.7	2.9
	P&S	1/14/99	59–79	25.1	65.4	1.9	2.6
DMW-7	DIF	1/13/99	69–70	30.9	2.4	8.5	1.3
	P&S	1/13/99	61–81	31.6	2.3	8.5	1.1 J
DMW-8	DIF	1/13/99	68–69	3.1	<.6	1.0 J	.3 J
	P&S	1/13/99	60–80	2.8	1.0	.7 J	.1 J
DMWD-3	DIF	1/13/99	161–162	3.2	4.0	<.1	.6 J
	P&S	1/14/99	155–175	3.3	4.0	<.1	.4 J
DMWD-14	DIF	1/14/99	153–154	2.5	1.6	.1 J	.4 J
	P&S	1/15/99	149–169	2.3	1.5	.0	.2 J
10-foot-long well screens							
DMWC-3	DIF	1/12/99	97–98	3.3	3.8	0.1 J	0.2 J
	P&S	1/12/99	93–103	4.6	5.8	.2 J	.3 J
DMWC-4	DIF	1/11/99	99–100	<.1	<.1	<.1	<.1
	P&S	1/11/99	95–105	.2 J	<.1	<.1	<.1
DMWD-10	DIF	1/12/99	166–167	5.0	2.7	<.1	.7 J
	P&S	1/12/99	162–172	4.6	2.8	<.1	.4 J
DMWD-1	DIF	1/11/99	156–157	<.1	<.1	<.1	<.1
	P&S	1/11/99	152–162	<.1	<.1	<.1	<.1
DMWD-11	DIF	1/11/99	175–176	<.1	<.1	<.1	<.1
	P&S	1/11/99	171–181	<.1	<.1	<.1	<.1
DPC-22	DIF	1/12/99	95–96	<.1	<.1	<.1	<.1
	P&S	1/13/99	91–101	<.1	<.1	<.1	<.1

RESULTS AND DISCUSSION

In most wells, the concentrations obtained by using downhole diffusion samplers closely matched those obtained using the purge-and-sample method (fig. 2). In 7 of the 14 wells (DMW-7, DMW-8, DMWC-3, DMWC-4, DMWD-10, DMWD-14, and DMWD-3), where VOC concentrations ranged from near the detection limit (0.1 µg/L) to 31.6 µg/L, the concentrations differed by only 2 µg/L or less between the two methods (table 2). For most regulatory

purposes, this difference is negligible. Of these wells, four had 20-ft-long well screens (wells DMW-7, DMW-8, DMWD-3, and DMWD-14), and the remaining had 10-ft-long well screens. No VOCs were detected in ground water collected from wells DMWD-1, DMWD-11, and DPC-22. The lack of VOC detection by either method in these wells indicates that the materials used in constructing the diffusion samplers did not contribute VOCs to the analytical results.

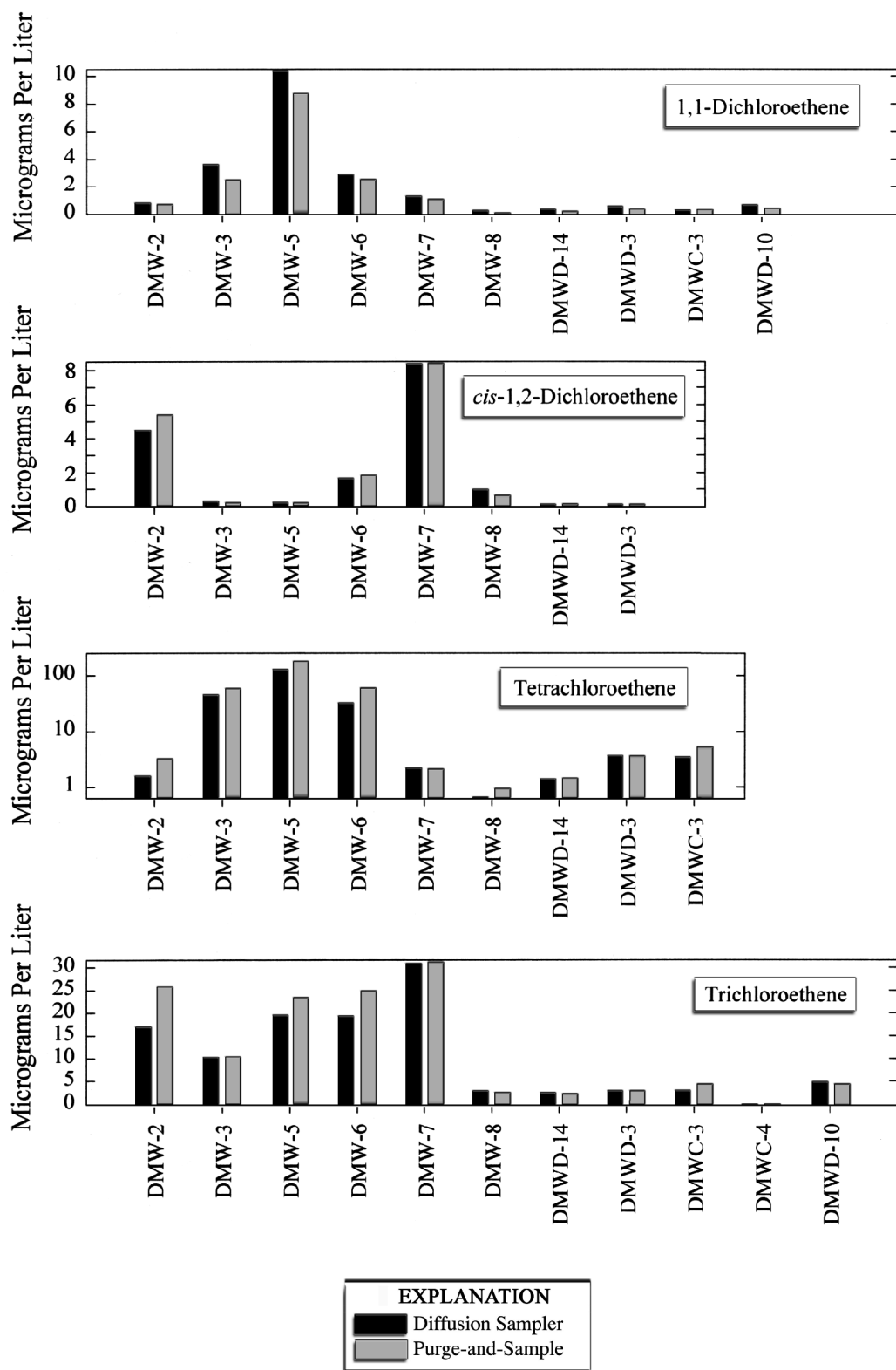


Figure 2. Comparison of volatile organic compound concentrations in ground water obtained from diffusion samplers and from the purge-and-sample method at Davis Global Communications, Sacramento, Calif., January 1999.

Analyses of ground water from the remaining four wells equipped with 20-ft-long screens (DMW-5, DMW-2, DMW-3, and DMW-6) indicated various degrees of comparability between the two sampling methods. In all four of these wells, where concentrations of individual VOCs were approximately 10 µg/L or less, comparisons between the two sampling methods showed differences of less than 2 µg/L. Although some of the comparisons in this low range of concentration values constitute a high percent difference, the actual difference in micrograms per liter is negligible for most regulatory purposes. For concentrations of trichloroethene (TCE) ranging from about 10 to 26 µg/L, the concentration differences also were small (ranging from about 4 to 6 µg/L in three of the wells and 8.7 µg/L in the fourth well, DMW-2). Greater differences were observed between the two methods for tetrachloroethene (PCE) concentrations above 30 µg/L. In wells DMW-3, DMW-5, and DMW-6, the differences were 23 percent (14.5 µg/L), 31 percent (66 µg/L), and 46 percent (30 µg/L), respectively (table 2).

Potential explanations for the differences between concentrations include insufficient well-equilibration time, water-level variations due to the intermittent pumping of onsite contaminant-removal wells, the possibility that the two methods sampled different water, and experimental errors inherent to each method. The hypothesis that insufficient well-equilibration time had elapsed following well testing and sampler installation seems unlikely because two of the three wells where the poorest matches were observed had not been subjected to borehole logging or pumping for electromagnetic flowmeter testing. It is possible, however, that intermittent pumping at nearby contaminant-removal wells during the equilibration period produced changes in hydraulic conditions at the screened intervals. Although contaminant-recovery wells typically operate continuously at the site, none were in operation on the day that geophysical logging and flowmeter testing were performed in well DMW-5 (December 15, 1998); some removal wells were in operation during part of the next day when well DMW-7 was tested; no removal wells were operating on the day that wells DMW-2 and DMW-8 were tested (December 17, 1998); and four removal wells were operating on the day that wells DMWD-3 and DMWD-14 were tested (December 18, 1998). Ground-water flow directions may vary substantially depending on when the contaminant-removal wells are in

operation. Because records of the times that the wells are on and off typically are not kept, it is possible that changes in the operation of contaminant-removal wells during the diffusion-sampler equilibration period resulted in hydraulic conditions that differed from the conditions at the time of sampling. This potentially could result in a discrepancy between the two sampling methods. Alternate explanations include the possibility of unrecorded changes in nearby contaminant-extraction well operation during the equilibration period.

Although insufficient equilibration time and changes in the operation of contaminant-removal wells potentially explain the discrepancies observed between sampling methods at some wells, water chemistry, geophysical logs, borehole flowmeter tests, and historical soil-gas data suggest a more probable scenario. Water chemistry from the diffusion samplers represents water derived from the screened interval, whereas the purge-and-sample method may have induced the infiltration of water from shallower zones above the well screen, thus resulting in the collection of mixed waters. A case in point is well DMW-5, where concentrations of TCE and PCE were higher in samples collected by purging the well than in samples collected by the diffusion samplers.

Analysis of water samples from the nine diffusion samplers positioned in the screened interval of well DMW-5 indicated that under static conditions of equilibration, the highest concentrations of TCE (19.8 µg/L) and PCE (145.0 µg/L) (table 2) in the diffusion samplers were from the center of the screened interval, which was the approximate center of an adjacent sand layer (fig. 3A, B, C). The data suggested that this sand layer was the predominant source of TCE and PCE to the well. However, TCE and PCE concentrations differed between the two sampling methods. TCE and PCE concentrations in water obtained by using the purge-and-sample method were 23.8 µg/L and 211.0 µg/L, respectively (table 2).

A probable explanation for the difference can be postulated by examining supportive data. Analysis of drilling logs and natural gamma logs indicated that the lower 13 ft of the screened interval of well DMW-5 was open to a sand layer extending from a depth of 67 to 80 ft below land surface (fig. 3C, D). Overlying the sand was a fractured silty clay with slickensided surfaces that extended from a depth of 38.5 to 61.5 ft below land surface; sand and gravel composed the remainder of the shallow subsurface. Flowmeter tests

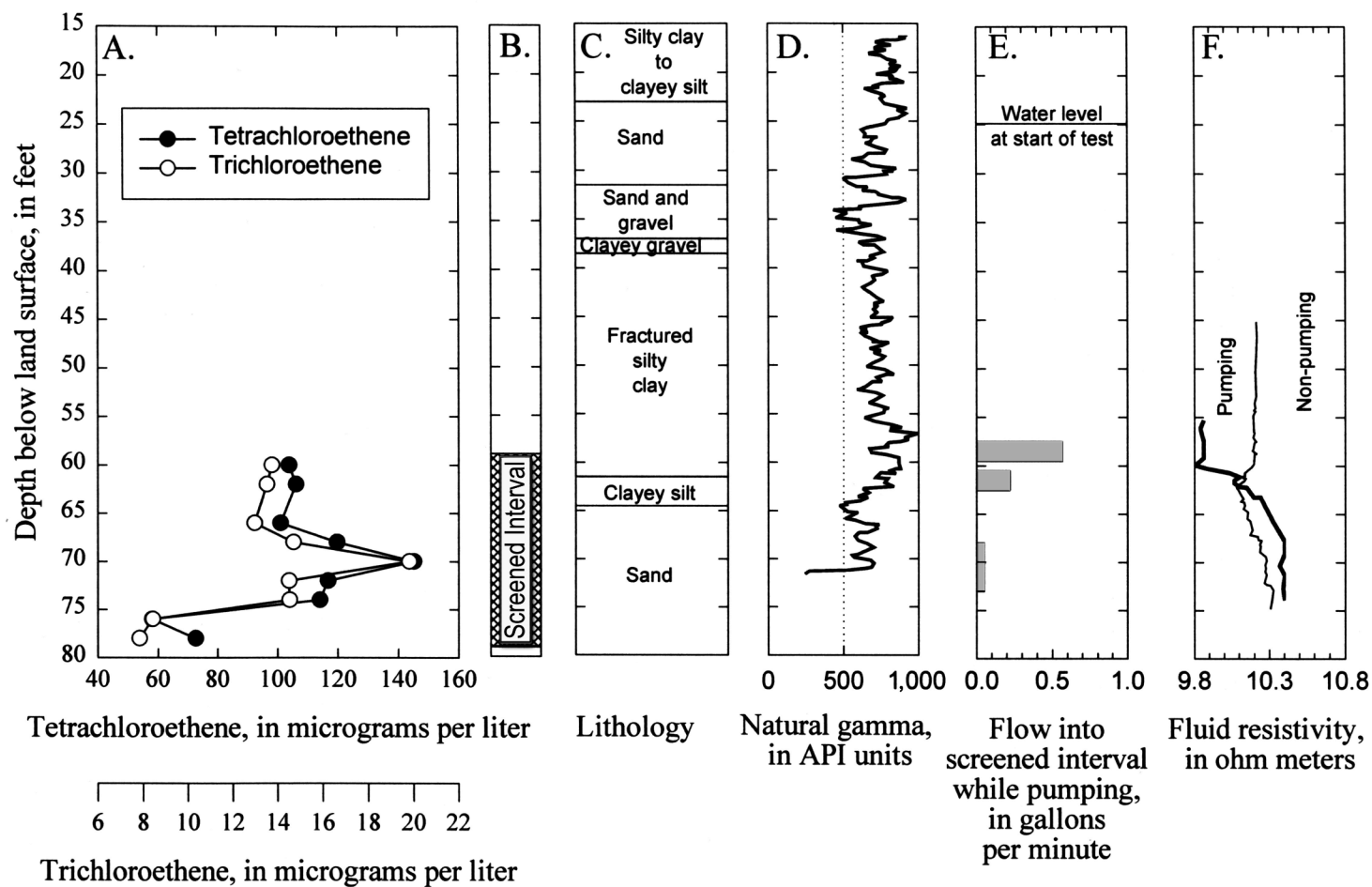


Figure 3. (A) Tetrachloroethene and trichloroethene concentrations in diffusion samplers, (B) screened interval, (C) lithology, (D) natural gamma, (E) borehole flowmeter, and (F) fluid-resistivity data at well DMW-5, Davis Global Communications, Sacramento, Calif., January 1999.

and geophysical logs run in the well indicated that when well DMW-5 was pumped, most of the water entered the well bore near the top of the screened interval at a depth of about 58 to 62 ft, with a smaller volume entering from the adjacent sand layer (fig. 3E). Under static conditions, however, the sand layer contributed the largest percentage of water moving into the screened interval (fig. 3E). Fluid resistivity logs provided further evidence that most water entered near the top of the well screen; during pumping, fluid resistivity increased sharply at the top of the screened interval (fig. 3F). The relatively high percentage of flow entering the well at the top of the screened interval during pumping suggests that purging the well may have induced the downward movement of water along the annular space of the well bore or along fractures within the silty clay material overlying the screened interval.

Results of a soil-gas survey conducted in 1994 showed that substantial amounts of TCE and PCE were

present at depths of 40 to 60 ft in the subsurface materials adjacent to well DMW-5 (CH2M HILL, 1995, site SGB-4). The presence of TCE and PCE in these shallow subsurface materials combined with the fact that pumping well DMW-5 created substantial drawdown, strongly suggests that pumping well DMW-5 resulted in the vertical downward movement of water into the screened interval and, ultimately, the mixing of water from shallower zones with water from the screened interval. Thus, the diffusion samplers probably provided a more representative sample of water from the screened interval.

Of the four wells showing VOC concentration differences that were greater than 2 µg/L between the two sampling methodologies, borehole flowmeter data were only available for wells DMW-5 and DMW-2. For well DMW-2, there were no substantial vertical variations in TCE concentrations within the well screen (fig. 4A, B). The borehole flowmeter data showed that when the well was pumped, approximately the same

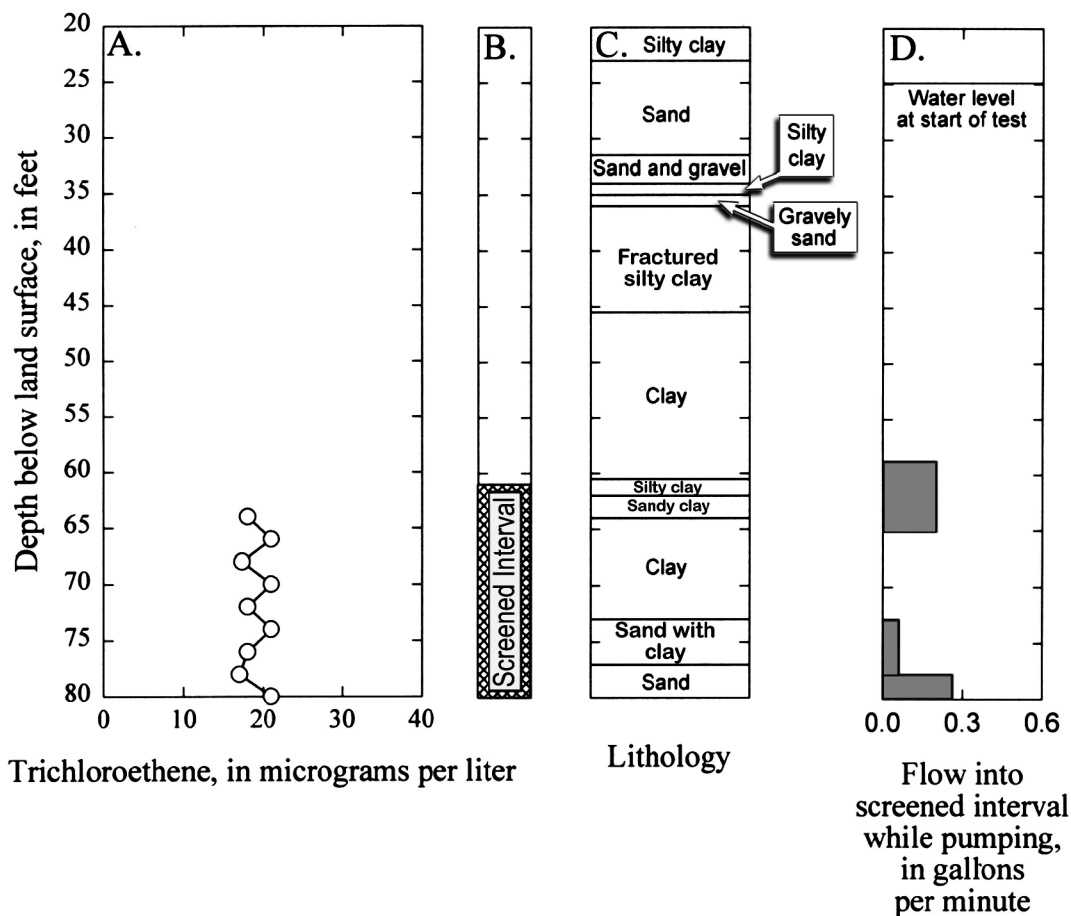


Figure 4. (A) Trichloroethene concentrations in diffusion samplers, (B) screened interval, (C) lithology, and (D) borehole flowmeter data at well DMW-2, Davis Global Communications, Sacramento, Calif., January 1999.

amount of water was obtained from the sand near the bottom of the screened interval as was obtained from the silty clay at the top of the screened interval (fig. 4C, D). As with well DMW-5, the apparent inflow of water from silty clay at the top of the well screen suggests that water may have moved downward from shallower zones to the screened interval along the annular space of the well bore or through fractures in the overlying material. Although no soil-gas profiles were collected at well DMW-2, soil-gas data from approximately 100 ft away showed the presence of TCE and PCE at depths of 40 and 60 ft (CH2M HILL, 1995, site SGB-8). Thus, as in well DMW-5, it is possible that the two methods sampled water from different sources at well DMW-2.

Wells DMW-3 and DMW-6 also showed lower PCE concentrations in the diffusion samplers than in water obtained by the purge-and-sample method

(table 2). No borehole flowmeter data were available for these wells, but the screened intervals for these wells were below fractured clay. The lithologic similarity between the sediment overlying the well screens in these wells with the sediment overlying the screens in wells DMW-5 and DMW-2 again implies the possibility that flow through fractures or the downward leakage of water from shallower zones during pumping influenced the water-quality samples from wells DMW-3 and DMW-6 (figs. 5, 6). At well DMW-6, when the well was not being pumped, the diffusion-sampler data imply that there was a concentration gradient in the screened interval with the highest concentrations occurring in a sand and fractured silt layer near the top of the screened interval.

The combined approach of using diffusion samplers and a borehole flowmeter also provided

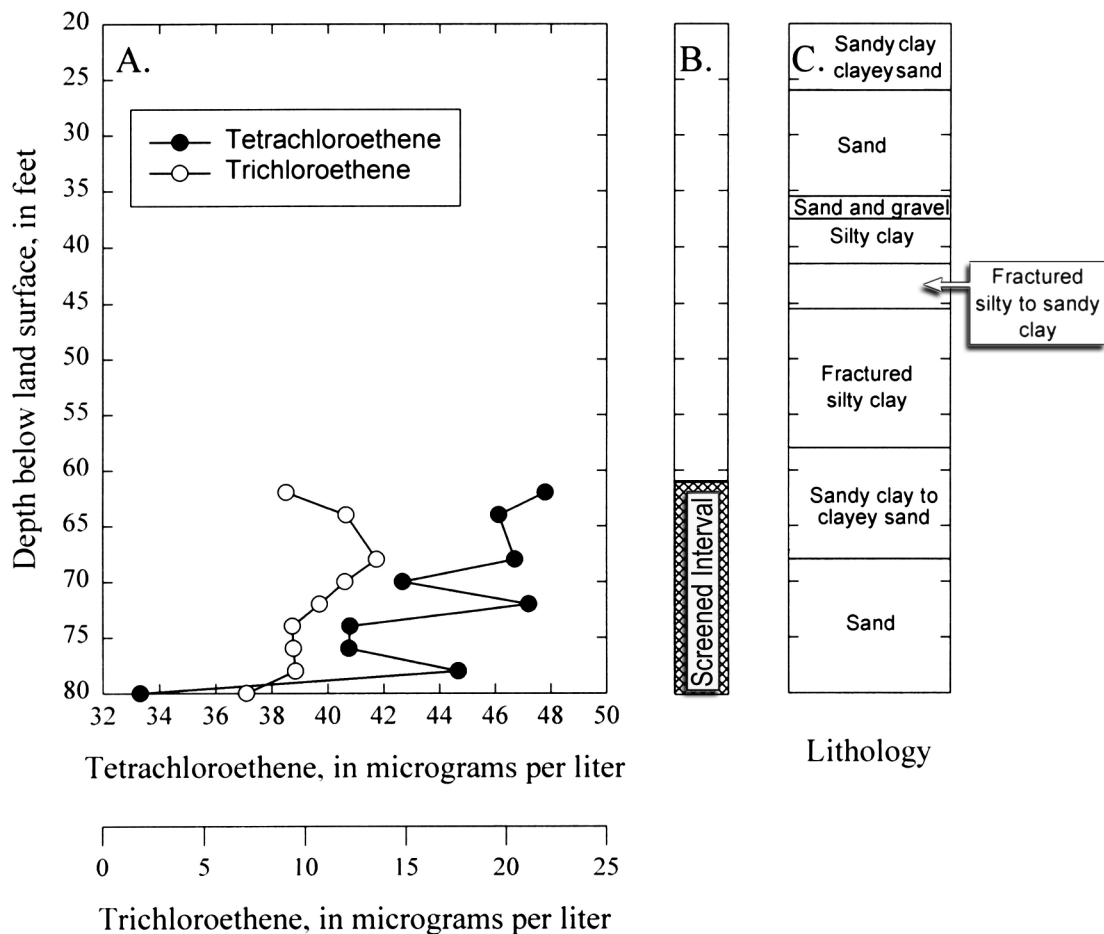


Figure 5. (A) Tetrachloroethene and trichloroethene concentrations in diffusion samplers, (B) screened interval, and (C) lithology at well DMW-3, Davis Global Communications, Sacramento, Calif., January 1999.

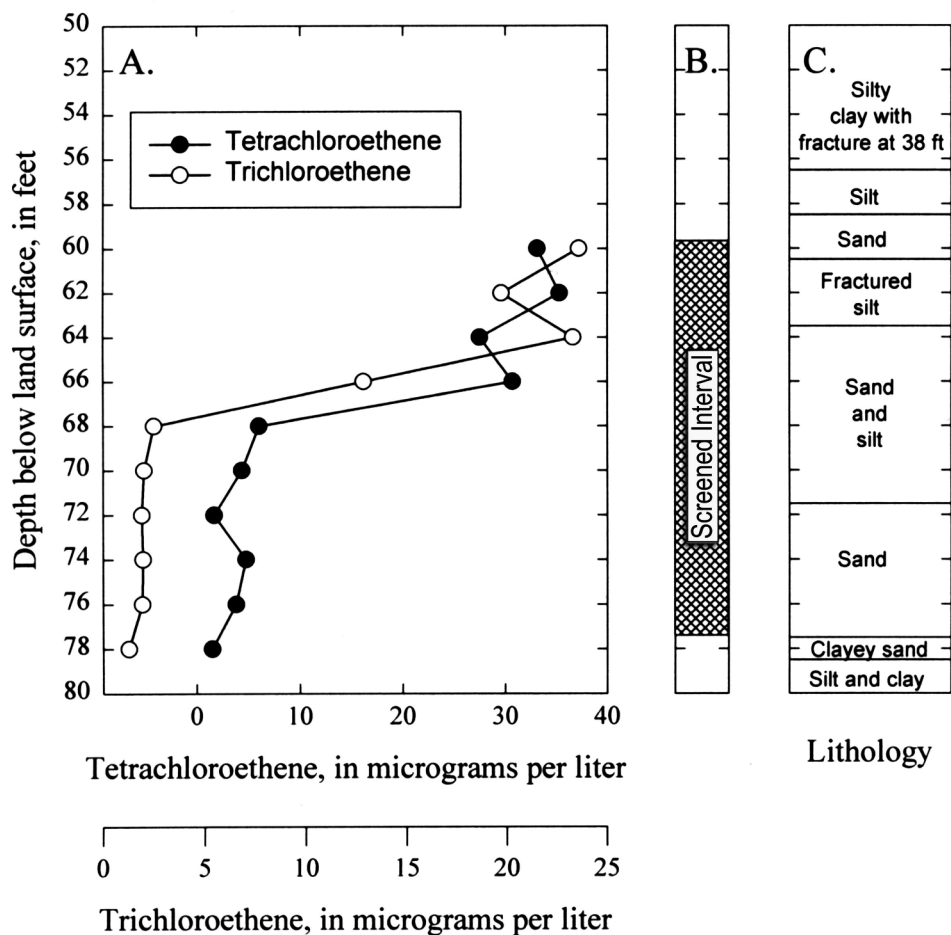


Figure 6. (A) Tetrachloroethene and trichloroethene concentrations in diffusion samplers, (B) screened interval, and (C) lithology at well DMW-6, Davis Global Communications, Sacramento, Calif., January 1999.

information on the source of water being removed from the aquifer by contaminant-removal wells in operation at the site. Water from well DMWD-3 contained low concentrations (less than 5 µg/L) of PCE and TCE in the screened interval, which was installed in a zone of sand and gravel (fig. 7A, B, C). Flowmeter tests conducted within the well, however, showed that water flowed into the well near the bottom of the screened interval and exited the well through the upper half of the screen, even when the well was not being pumped (fig. 7D). When a pump was placed in the well and water was pumped out at 0.96 gallon per minute, water still exited the well through the upper part of the screened interval. A probable explanation is that contaminant-removal well DEWC-3, which was 32.4 ft

south of well DMWD-3, pumped water from a depth of 93–108 ft below land surface and may have caused the flowthrough by capturing water from the horizon screened by well DMWD-3. Because the water in well DMWD-3 contained less than 5 µg/L of the target compounds, the data suggest that some of the water captured by contaminant-removal well DEWC-3 was relatively uncontaminated. Thus, a combination of diffusion samplers and borehole flowmeter tests may be useful in optimizing the contaminant-capture radius of contaminant-removal wells. Overall, the data suggest that the use of diffusion samplers provides an alternative sampling method to the purge-and-sample approach used for ground-water investigations.

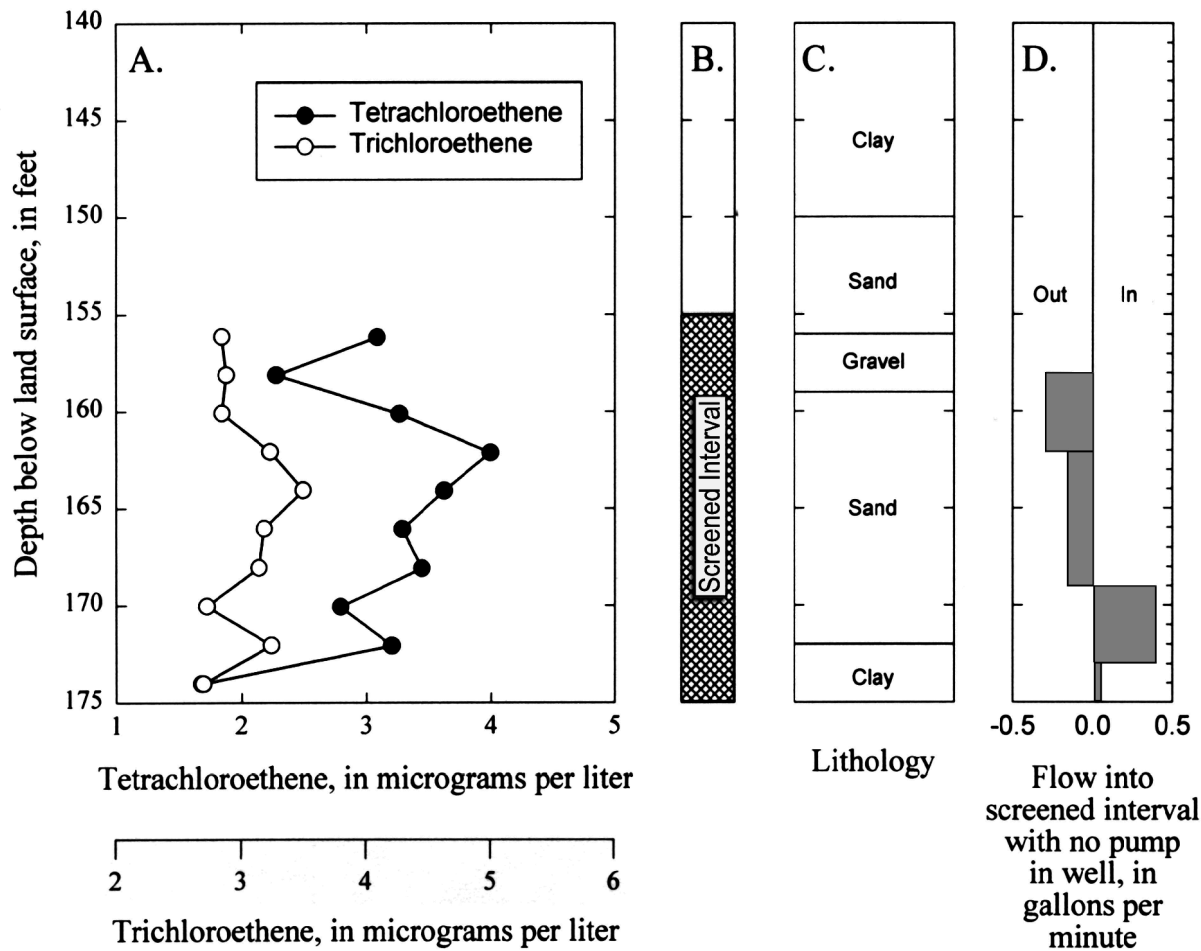


Figure 7. (A) Tetrachloroethene and trichloroethene concentrations in diffusion samplers, (B) screened interval, (C) lithology, and (D) borehole flowmeter data at well DMWD-3, Davis Global Communications, Sacramento, Calif., January 1999.

SUMMARY

Fourteen wells were instrumented with diffusion samplers at Davis Global Communications, Sacramento, Calif., as a test to determine whether the samplers could be used to obtain representative volatile organic compound (VOC) concentrations at the site. Of these wells, eight had screen lengths of 20 ft and two had screen lengths of 10 ft. Single diffusion samplers were placed in the 10-ft-long well screens, and multiple diffusion samplers were placed in the longer screens. The samplers were recovered after a minimum of 14 days, and the wells were then sampled by using the purge-and-sample method.

In most wells, the concentrations obtained by using downhole diffusion samplers closely matched those obtained by using the purge-and-sample method.

In seven wells, the concentrations differed between the two methods by only 2 µg/L or less. For most regulatory purposes, this difference is negligible. In three of the remaining wells, VOCs were not detected in water obtained by using either method.

In the remaining four wells, the degree of comparability between the two sampling methods varied. In these wells, differences between the methods were less than 2 µg/L in the 0.2- to 8.5-µg/L concentration range and from 1.2 to 8.7 µg/L in the 10- to 26-µg/L concentration range. In wells DMW-3, DMW-5, and DMW-6, greater differences (23 percent or 14.5 µg/L, 31 percent or 66 µg/L, and 46 percent or 30 µg/L, respectively) between the two methods were observed for PCE concentrations which ranged between 30 and 211 µg/L.

Potential explanations for the differences include insufficient equilibration time for the diffusion samplers, hydraulic changes during the equilibration period due to possible unrecorded changes in the pumping of onsite contaminant-removal wells, and the possibility that the two methods sampled water from differing sources at some wells. Data collected during this investigation, combined with soil-gas data collected during a previous investigation, implied that at some wells, the two methods sampled water from differing horizons.

At wells DMW-2 and DMW-5, the diffusion samplers seemed to be sampling water representative of the horizon adjacent to the screened interval. Lithologic data, borehole fluid resistivity and natural gamma logs, borehole flowmeter results, water-level measurements, and historical soil-gas data suggest, however, that water obtained while using the purge-and-sampling method at wells DMW-2 and DMW-5 was derived partly from the downward movement of water along the annular space of the well bore or through fractures in the silty clay. Although borehole flowmeter data were not available for the remaining two wells (DMW-3 and DMW-6), the lithologic similarity between the sediments at these wells and the sediments at wells DMW-2 and DMW-5 implied that water could move downward from shallower zones into the well screen while using the purge-and-sample method. Thus, as in this case, the purge-and-sample approach may have overestimated concentrations in the screened interval. Overall, the data suggest that the use of diffusion samplers provided an alternative sampling

method to the purge-and-sample approach used for ground-water investigations.

The data also showed that vertical variations in VOC concentrations can exist within the screened intervals. In addition, the combined use of borehole flowmeter tests and diffusion samplers showed that contaminant-removal well DEWC-3 seemed to be capturing water from the horizon screened by well DMWD-3, indicating that at least some of the water captured by contaminant-removal well DMWC-3 contains VOC concentrations less than 5 µg/L. These data may be useful in optimizing the radius of capture of contaminated ground water by the contaminant-removal wells.

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Field Testing of Passive Diffusion Bag Samplers for Collection of
Ground-Water Volatile Organic Compound Concentrations at
Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota,
November 1999 to May 2000

USGS Water-Resources Investigations Report 00-4246

By Don A. Vroblesky and Matthew D. Petkewich

Field Testing of Passive Diffusion Bag Samplers for Volatile Organic Compound Concentrations in Ground Water, Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota, November 1999 and May 2000

By Don A. Vroblesky and Matthew D. Petkewich

ABSTRACT

Volatile organic compound concentrations from passive diffusion bag samplers were compared with concentrations from conventional purge (three or more casing volumes) sampling and low-flow purge sampling in side-by-side tests in 17 wells at the Naval Industrial Reserve Ordnance Plant, in Fridley, Minnesota. An initial comparison of 1,2-dichloroethene and trichloroethene concentrations obtained by using passive diffusion bag samplers and the conventional purge method in wells where one passive diffusion bag sampler was deployed showed good agreement at several wells but poor agreement at others. Collection of data from multiple diffusion samplers during the conventional purge sampling and during the low-flow sampling, however, suggests that the volatile organic compound concentrations from the passive diffusion bag samplers accurately reflect the volatile organic compound distribution in the screened interval, whereas the conventional purge and low-flow purge samples reflect mixing during pumping. The data also show that contaminant stratification was present in some wells. In one well, trichloroethene concentrations ranged from 470 to 1,600 micrograms per liter over a vertical distance of approximately 6 feet.

INTRODUCTION

Low-density polyethylene passive diffusion bag (PDB) samplers, filled with deionized water or air, can be an inexpensive alternative sampling method for volatile organic compounds (VOCs) in contaminated wells (Vroblesky and Hyde, 1997; Gefell and others, 1999). The use of PDB samplers in wells has generated interest because they can be used to sample ground water without the need for prior well purging. Investigations have shown that PDB sampling methods can result in substantial cost savings over traditional sampling methods (Parsons Engineering Science Inc., 1999; McClellan AFB Environmental Directorate, 2000).

The Naval Industrial Reserve Ordnance Plant (NIROP), in Fridley, Minnesota, has been in operation since 1940. Activities at the plant resulted in ground-water contamination by chlorinated aliphatic hydrocarbons, primarily trichloroethene (TCE). The TCE contamination has migrated from the NIROP property and probably extends to the Mississippi River (fig. 1) (Tetra Tech NUS, Inc., 2000). As part of an effort to reduce long-term monitoring costs associated with well sampling, Southern Division Naval Facilities Engineering Command requested the U.S. Geological Survey to examine the potential for using PDB samplers as a low-cost alternative to the standard sampling approaches used at the site.

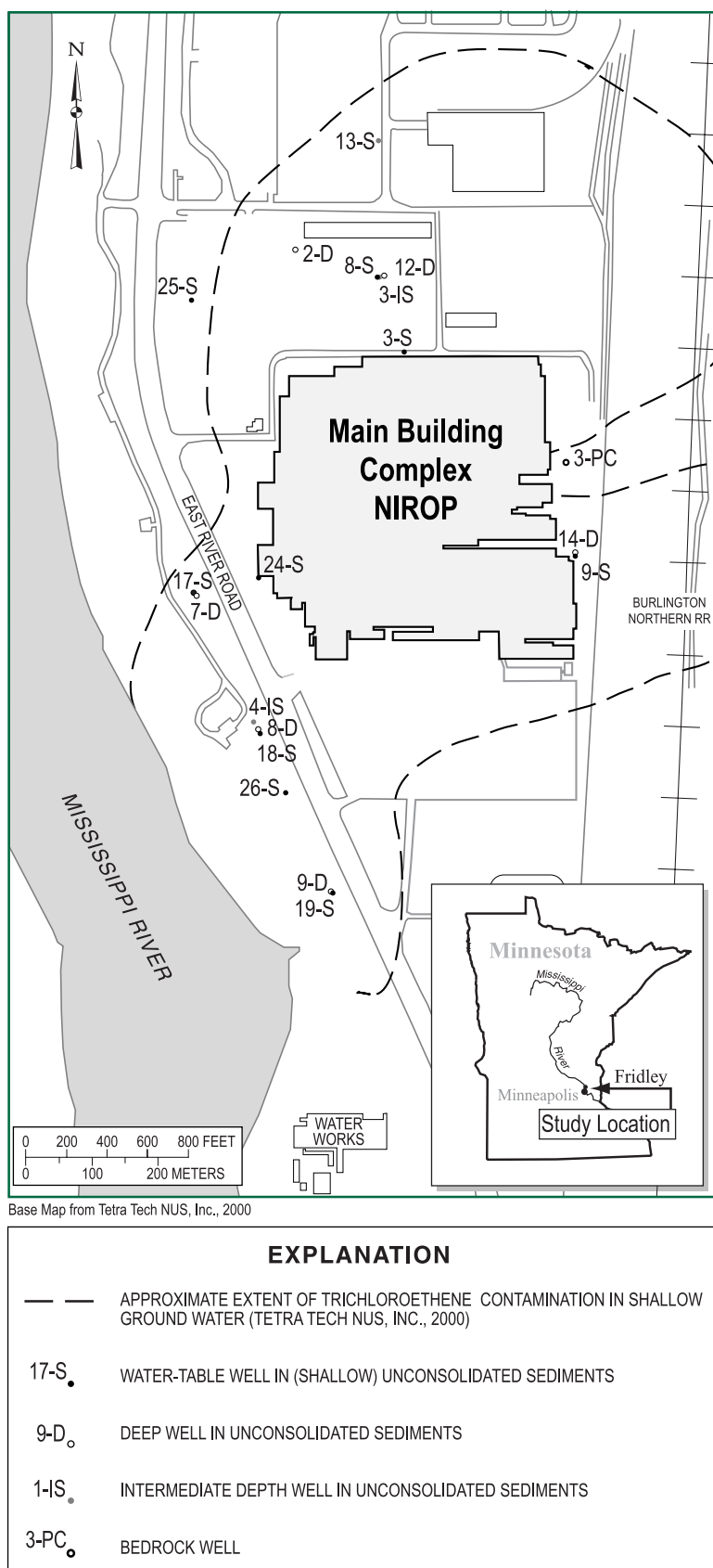
The uppermost aquifer system at NIROP consists of heterogeneous interbedded medium- to coarse-grained sands with layers of fine-grained sand

and gravel and low-permeability sediment layers ranging from silt to clay. The uppermost aquifer is referred to as an aquifer system because it can be roughly divided into two water-bearing zones varying substantially in thickness and hydraulic connection across the site. The shallowest zone ranges in thickness from 41 to 93 feet (ft), and the deeper zone ranges in thickness from 19 to 55 ft (Tetra Tech NUS, Inc., 2000). Most of the wells tested during this investigation are screened in this aquifer system. Beneath the uppermost aquifer system, and separated from it by a leaky confining unit, is a bedrock dolomitic limestone that functions as an aquifer; well 3-PC was open to this aquifer (fig. 1).

Purpose and Scope

The purpose of this report is to present the findings of an investigation to determine whether the use of PDB samplers is a viable VOC sampling method for observation wells at the site. The investigation involved comparing VOC concentrations in water obtained by using PDB samplers with VOC concentrations in water obtained by using the conventional purge-and-sample method routinely used at the site. In addition, VOC concentrations in water from PDB samples from selected wells collected with PDB samplers were compared with VOC concentrations in water obtained by low-flow sampling. PDB samplers were placed in 19 observation wells. Multiple PDB samplers were placed in 8 of the wells.

Figure 1. Locations of sampling sites at the Naval Industrial Reserve Ordnance Plant (NIROP), Fridley, Minnesota, November 1999 to May 2000.



Acknowledgments

This investigation was funded by the U.S. Navy, Southern Division, Naval Facilities Engineering Command.

METHODS

Each PDB sampler consisted of a 2-inch diameter low-density polyethylene (LDPE) tube containing deionized water and heat-sealed at both ends. On the outside of each sampler, LDPE mesh provided abrasion protection. This sampling method is patented (patent number 5,804,743) and is available for nonexclusive licensing from the U.S. Geological Survey Technology Enterprise Office, MS-211, National Center, 12201 Sunrise Valley Drive, Reston, Virginia (telephone 703-648-4450; fax 703-648-4408).

PDB samplers were attached to weighted lines by plastic cable ties. In most wells, single PDB samplers were deployed at the approximate vertical centers of the saturated screened intervals.

PDB samplers were tested in 19 wells at NIROP (table 1; fig. 1). During the initial test, the samplers were deployed in October 1999, allowed to equilibrate approximately 30 days, and recovered in November 1999. Seventeen of the wells were instrumented with single PDB samplers, and two wells were instrumented with multiple PDB samplers. In a second test, multiple PDB samplers were deployed in seven wells in April 2000, allowed to equilibrate approximately 35 days, and recovered in May 2000.

Recovery of the PDB samplers consisted of removing them from the wells, cutting them open, and decanting the water into 40-milliliter (mL) volatile organic analysis (VOA) vials. The samples were preserved with hydrochloric acid, stored at approximately 4 degrees Celsius (°C), and transferred to a commercial laboratory for analysis using the U.S. Environmental Protection Agency (USEPA) method 8260b (U.S. Environmental Protection Agency, 1999).

During the November 1999 test, the wells were purged and sampled by the site contractor using the method typical for the site. This method consisted of first purging each well by removing at least three casing volumes of water and monitoring until the pH, specific conductance, and temperature stabilized. In well 12-D (fig. 1; table 1), this involved removing 300 gallons of water (four casing

Table 1. Well-construction details and number of passive diffusion bag samplers deployed, Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota

[PDB, passive diffusion bag; DU, deep unconsolidated sediments; MU, middle unconsolidated sediments; DLS; deep limestone; SU, shallow unconsolidated sediments; NA, data not available]

Well number (fig. 1)	Screen length (feet)	Screened depth below top of casing (feet)		Zone	Number of PDB samplers deployed	
		Top	Bottom		Test 1 (1999)	Test 2 (2000)
2-D	10	102.3	112.5	DU	1	0
3-IS	10	67.4	77.4	MU	1	0
3-PC	27	132.9	159.6	DLS	6	6
3-S	15	19.7	34.8	SU	1	9
4-IS	10	66.9	76.9	MU	1	0
7-D	10	108	118	DU	1	0
8-D	10	118	128	DU	1	6
8-S	10	19.8	29.7	SU	1	4
9-D	10	114.3	124.3	DU	1	0
9-S	10	19.3	29.3	SU	1	0
12-D	10	122.9	132.9	DU	1	0
13-S	10	23.9	33.9	SU	1	0
14-D	10	82.6	92.6	DU	1	0
17-S	10	29	39	SU	1	0
18-S	10	30.8	40.8	SU	1	6
19-S	10	35	45	SU	1	5
24-S	15	21.7	36.7	SU	3	0
25-S	10	NA	NA	SU	1	0
26-S	NA	NA	NA	SU	1	5

volumes). Once the well was purged, water samples for VOC analysis were collected by using the pump and then sent for analysis using USEPA method 8260b (U.S. Environmental Protection Agency, 1999) to the same laboratory that analyzed the PDB samplers.

A second test (April to May 2000) was done to provide further information in wells showing poor agreement. During the second test, VOC concentrations in multiple PDB samplers were compared with VOC concentrations collected by using low-flow methods.

The low-flow sampling approach (Barcelona and others, 1994; Shanklin and others, 1995) was used to reduce mixing due to the removal of large quantities of water during the purging process. Low-flow sampling for the second test consisted of pumping the wells at a rate of approximately 100 to 300 mL per minute until the temperature, pH, and specific conductance stabilized and no additional water-level drawdowns were observed. Typically, this required purging less than a gallon of water over a time period of approximately 15 minutes.

Four to nine PDB samplers were deployed in each of the seven wells during the second test. At all of the tested wells except well 3-S, a submersible positive-displacement pump was deployed at the same time as the PDB samplers. In well 3-S, an obstruction in the well prevented installation of the pump; therefore, a Tygon tube was attached to the PDB-sampler line at the time of sampler deployment. One end of the tube was open at the depth of the PDB sampler, and the other end extended to the surface for attachment to a peristaltic pump.

After field-parameter stabilization, water samples were collected for VOC analysis. The submersible pumps then were removed from the wells with the attached PDB samplers, and the water recovered in the PDB samplers was transferred to VOA vials. Both sets of samples were sent to a commercial laboratory for analysis using USEPA method 8260b (U.S. Environmental

Protection Agency, 1999). The same general approach was used to sample well 3-S; however, well 3-S was sampled by low-flow methodology using a peristaltic pump.

FIELD TEST RESULTS AND CONCLUSIONS

A comparison of total 1,2-dichloroethene (1,2-DCE) and TCE concentrations obtained by using PDB samplers to concentrations obtained by using the conventional purge method in wells where one PDB sampler was deployed showed good agreement at several wells and poor agreement in others (table 2). For this investigation, good agreement was considered to be a concentration difference of less than 5 micrograms per liter ($\mu\text{g/L}$) for 1,2-DCE and to be a concentration difference of either less than 10 $\mu\text{g/L}$ or less than 10 percent for TCE. Of the sites

Table 2. Comparison of total 1,2 dichloroethene and trichloroethene concentrations obtained by purge-and-sample method to concentrations obtained by using passive diffusion bag samplers in wells where a single passive diffusion sampler was deployed at the Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota, November 1999

[1,2-DCE, total 1,2-dichloroethene; TCE, trichloroethene; PDB, passive diffusion bag; <, less than; >, greater than. Samples obtained by the purge-and-sample method were collected by a private consultant. Concentrations are in micrograms per liter ($\mu\text{g/L}$)]

Well number (fig. 1)	Sample date	1,2-DCE concentration		TCE concentration		Well volumes purged	Gallons of water purged
		PDB-sampling method	Purge-and-sample method	PDB-sampling method	Purge-and-sample method		
2-D	11/3/99	2.8	3.1	2.5	4.4	3	54
3-IS	11/3/99	6.4	4.2	69	42 [#]	4	40
3-S	11/3/99	3.7	260 [#]	38	730 [#]	4	6
4-IS	11/4/99	53	57	860	910	3	27
7-D	11/3/99	<1	4.4	2.2	17 [#]	3	180
8-D	11/4/99	52	12 [#]	23	70 [#]	4	260
8-S	11/3/99	440	620 [#]	240	340 [#]	4	8
9-D	11/3/99	10	9.1	68	62	4	240
9-S	11/3/99	22	19	180	160 [#]	5	10
12-D	11/3/99	22	2 [#]	14	24	4	300
13-S	11/2/99	<2	<2	<1	<1	3	9
14-D	11/2/99	<2	<2	<1	<1	3	156
17-S	11/3/99	71	68	40	42	3	9
18-S	11/4/99	130	650 [#]	570	2,300 [#]	4	12
19-S	11/3/99	15	19	410	610 [#]	3	6
25-S	11/2/99	<2	<2	<1	<1	3	9
26-S	11/4/99	52	38 [#]	2,900	3,800 [#]	3	6

[#]Sites that showed poor comparison between methods (>5 $\mu\text{g/L}$ difference between methods for total 1,2-DCE, >10 $\mu\text{g/L}$ or >10 percent difference between methods for TCE).

that did not meet these criteria, samples from well 3-IS had higher 1,2-DCE and TCE concentrations in water from the PDB sampler than from the pumped sample, implying that higher concentrations were present in the well than were indicated by the pumped sample, and the PDB sampler better represented the higher concentrations. Samples from well 9-S had TCE concentrations that differed by 11 percent, but the concentration was higher in water from the PDB sampler than from the pumped sample, again implying that the PDB sampler better represented the higher concentrations. Samples from well 7-D had higher concentrations of TCE in water from the purged sample than in water from the PDB sample (table 2); however, some differences probably are to be expected after purging 180 gallons of water from the well.

Other wells showed substantially poorer agreement in VOC concentrations between the PDB samples and the conventional purge samples. In particular, wells 3-S, 8-S, 18-S, 19-S, and 26-S showed substantially higher VOC concentrations in water from the conventional purge sampling than in water from the PDB samplers (table 2). Examination

of the data from two wells where multiple diffusion samplers were deployed during the first test (table 3) provides some clues as to a possible source of the poor agreement in some of the wells. At well 24-S, the analytical data show no significant concentration difference between sampling methods for 1,1-dichloroethane (1,1-DCA), 1,1-dichloroethene (1,1-DCE), 1,2-DCE, and TCE. Data from the PDB sampler, however, indicates the presence of relatively high 1,2-DCE concentrations and relatively low TCE concentrations near the top of the screen and the opposite near the base of the screen (fig. 2A). This may mean that the dechlorination potential is higher in sediment near the base of the screen than near the top of the screen or it may be the product of differential transport. In any case, it is apparent that the 1,2-DCE and TCE concentrations change over the screened interval. Thus, pumping the well would lead to mixing of these differing concentrations. Although the 1,2-DCE and TCE concentrations obtained by the conventional purging approach differs from the concentrations found in the PDB sampler from the same depth, it appears that the pumped sample represents an approximate average concentration across the screened interval (fig. 2A, table 3). The data suggest that some of the differences in results between the two methods may be from mixing of stratified contaminant concentrations by the purging of three or more casing volumes.

At well 3-PC, no contaminant stratification was apparent from the PDB-sampler data (fig. 2B); however, the tetrachloroethene (PCE) concentrations from the PDB sampler were approximately 15 µg/L lower than in water from the pumped sample. After purging 285 gallons of water, the contributing areas and sources of water sampled are probably much different between the conventional purged sample and waters in contact with the PDB sampler, thus leading to differences in concentrations of PCE. TCE and 1,2-DCE were not significant components in the contamination at well 3-PC.

Table 3. Concentrations of selected volatile organic compounds in water from multiple passive diffusion bag samplers and conventional purge sampling, Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota, November 1999

[1,1-DCA, 1,1-dichloroethane; 1,1-DCE, 1,1-dichloroethene; 1,2-DCE, total 1,2-dichloroethene; PCE, tetrachloroethene; TCE, trichloroethene; PDB, passive diffusion bag sampler; P&S, conventional purge-and-sample method (samples were collected by private consultant); <, less than. Concentrations are in micrograms per liter]

Well number (fig. 1)	Sampling method	Depth below top of casing (feet)	1,1-DCA	1,1-DCE	1,2-DCE	PCE	TCE
3-PC	PDB	134.8	<1	<1	<2	22	1.7
3-PC	PDB	138.8	<1	<1	<2	23	1.7
3-PC	PDB	142.8	<1	<1	<2	25	1.7
3-PC	PDB	146.8	<1	<1	<2	24	1.7
3-PC	PDB	150.8	<1	<1	<2	24	1.6
3-PC	PDB	154.8	<1	<1	<2	25	1
3-PC	P&S	144.7	<1	<1	<2	40	2.7
24-S	PDB	24.3	3.5	1.9	780	<1	200
24-S	PDB	28.3	3.6	2.1	600	<1	350
24-S	PDB	32.3	2.4	1.4	380	<1	500
24-S	P&S	28.3	3.4	1.6	520	<1	330

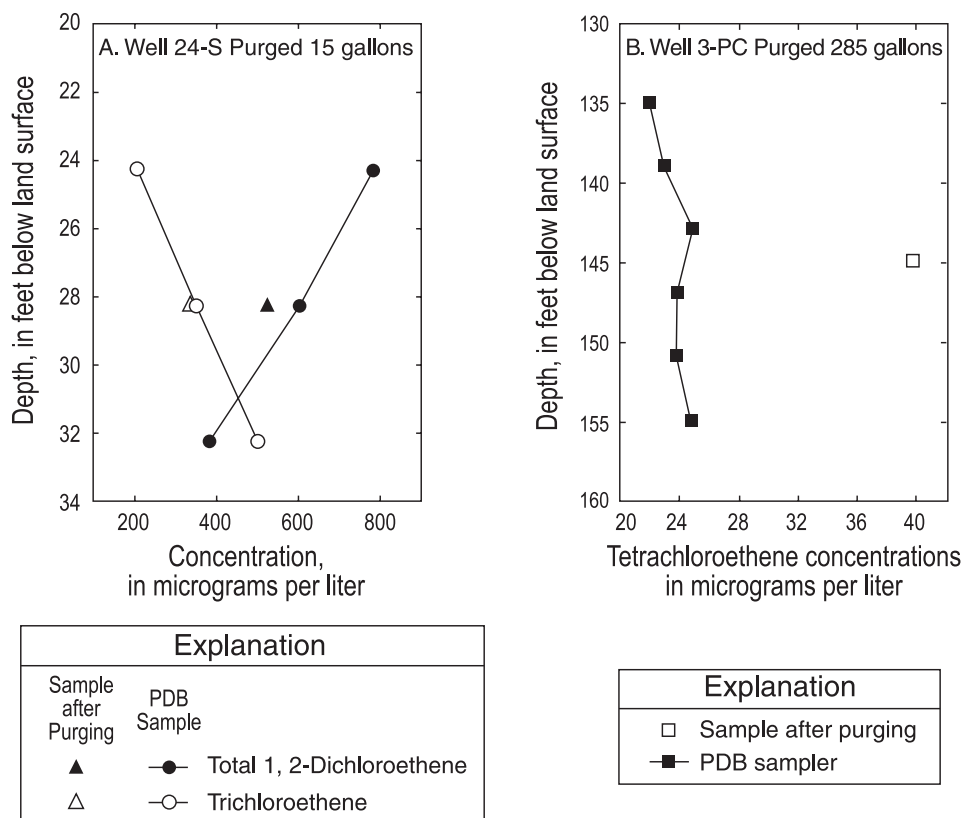


Figure 2. Comparison between passive diffusion bag (PDB) sampling method and conventional purge sampling method, Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota, November 1999.

To determine whether the differences between the methods could be attributed to mixing as a result of the conventional purging approach, seven of the wells where poor agreement was observed were resampled by using a combination of multiple PDB samplers and a low-flow purging method (table 4). At well 3-PC, where PCE concentrations differed by 15 µg/L between the conventional purge and the PDB samplers, resampling showed that the PCE concentrations in water from the PDB samplers and the low-flow sampling differed by only about 2 µg/L. These data suggest that purging 285 gallons during the first sampling adversely affected the results.

Well 18-S showed substantial differences in concentration between methods during the first sampling (table 2). Concentrations of 1,2-DCE and TCE were 650 and 2,300 µg/L, respectively, in water from the conventional purge method but only 130 and 570 µg/L, respectively, in water from the PDB sampler (table 2). During the second sampling, the PDB samplers showed that substantial stratification of VOCs is present over a vertical interval of

approximately 6 ft (fig. 3A). TCE concentrations ranged from 470 µg/L at a depth of 31.48 ft to 1,600 µg/L at a depth of 37.61 ft (table 4). The 1,2-DCE concentration changed from 240 to 480 µg/L over the same interval. Although the TCE concentration from the low-flow sampling (1,000 µg/L) differs from the closest PDB samplers (1,300 and 1,600 µg/L), the low-flow-sampling concentrations are consistent with what would be expected from mixing the concentrations over the screened interval during pumping (fig. 3A). During the first round of sampling, the PDB sampler was positioned in the center of the well screen in an area where concentrations were substantially lower than near the base of the screened interval. Therefore, mixing of water across the screened interval during pumping could produce pumped concentrations exceeding those in the single PDB sampler, as shown in table 2. The data suggest that the VOC concentrations from the PDB samplers accurately reflect the VOC distribution in the screened interval. The data also suggest that the discrepancy between PDB, conventional

Table 4. Concentrations of selected volatile organic compounds in water from diffusion and low-flow sampling, Naval Industrial Ordnance Reserve Plant, Fridley, Minnesota, May 2000

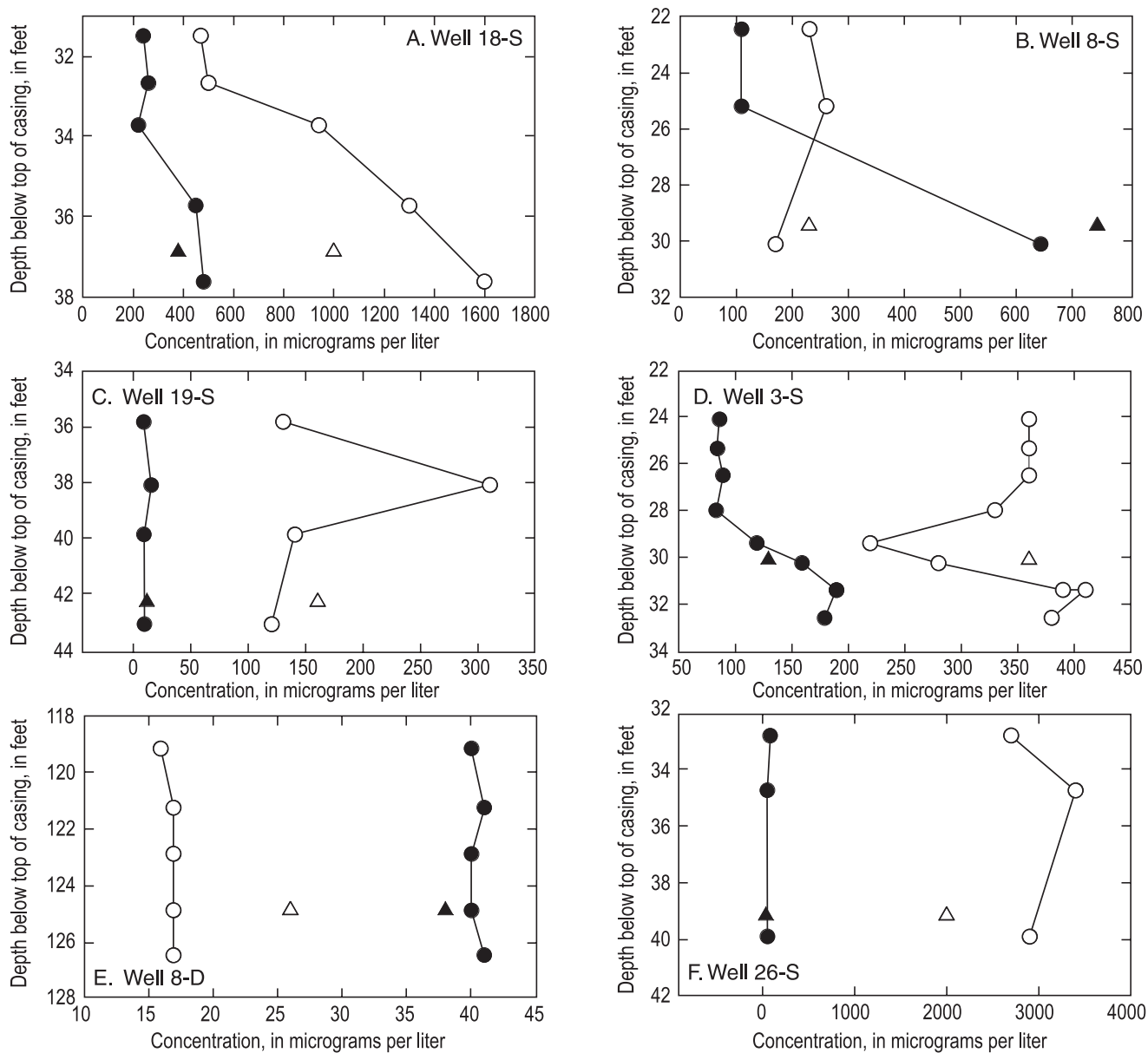
[1,1,1-TCA, 1,1,1-trichloroethane; 1,1-DCA, 1,1-dichloroethane; 1,2-DCE, 1,2-total dichloroethene; PCE, tetrachloroethene; TCE, trichloroethene; PDB, passive diffusion bag; LF, low-flow; <, less than. Concentrations are in micrograms per liter]

Well	Sampling method	Depth below top of casing (feet)	1,1,1-TCA	1,1-DCA	1,2-DCE	Benzene	PCE	TCE
3-PC	PDB	135.6	<1.0	<1.0	<2.0	<1.0	8.3	1.6
3-PC	PDB	140.2	<1.0	<1.0	<2.0	<1.0	8.5	1.5
3-PC	PDB	145.3	<1.0	<1.0	<2.0	<1.0	8.8	1.7
3-PC	PDB	150.2	<1.0	<1.0	<2.0	<1.0	8.9	1.6
3-PC	PDB	157.1	<1.0	<1.0	<2.0	<1.0	9.5	1.7
3-PC	LF ⁺	157.6	<1.0	<1.0	<2.0	<1.0	11	1.3
3-S	PDB	24.11	22	4.2	87	<2.0	<2.0	360
3-S	PDB	25.36	21	4.5	85	<2.0	<2.0	360
3-S	PDB	26.51	21	4.6	90	<2.0	<2.0	360
3-S	PDB	28.01	17	5	84	<2.0	<2.0	330
3-S	PDB	29.41	5.3	10	120	<2.0	<2.0	220
3-S	PDB	30.26	<2.0	16	160	<2.0	<2.0	280
3-S	PDB	31.41	<2.0	15	190	<2.0	2.5	390
3-S ^R	PDB	31.41	<2.0	15	190	<2.0	2.8	410
3-S	PDB	32.61	<5.0	<5.0	180	<5.0	<5.0	380
3-S	LF [#]	30.11	15	8.3	130	<2.0	<2.0	360
8-D	PDB	119.1	<1.0	1	40	5	<1.0	16
8-D	PDB	121.2	<1.0	1.1	41	5	<1.0	17
8-D	PDB	122.9	<1.0	1	40	4.8	<1.0	17
8-D	PDB	124.9	<1.0	1	40	4.9	<1.0	17
8-D	PDB	126.5	<1.0	1.1	41	4.8	<1.0	17
8-D	LF ⁺	124.9	<1.0	1.1	38	3.1	1.1	26
8-S	PDB	22.45	<2.0	<2.0	110	<2.0	3.5	230
8-S	PDB	25.2	<2.0	<2.0	110	<2.0	3.9	260
8-S	PDB	30.1	<5.0	<5.0	640	<5.0	<5.0	170
8-S	LF ⁺	29.45	<10	<10	740	<10	<10	230
18-S	PDB	31.48	<5.0	<5.0	240	<5.0	<5.0	470
18-S	PDB	32.66	<5.0	<5.0	260	<5.0	<5.0	500
18-S	PDB	33.71	<10	<10	220	<10	<10	940
18-S	PDB	35.71	<10	<10	450	<10	<10	1,300
18-S	PDB	37.61	<10	<10	480	<10	<10	1,600
18-S	LF ⁺	36.86	<10	<10	380	<10	<10	1,000
19-S	PDB	35.86	<1.0	3.1	8.5	<1.0	3.1	130
19-S	PDB	38.11	<2.0	3.4	15	<2.0	<2.0	310
19-S	PDB	39.86	<1.0	2.9	8.7	<1.0	2.8	140
19-S	PDB	43.06	<1.0	3.5	9.1	<1.0	3.1	120
19-S	LF ⁺	42.26	<1.0	2.6	11	<1.0	2.4	160
26-S	PDB	32.76	<20	<20	86	<20	<20	2,700
26-S	PDB	34.71	<20	<20	53	<20	<20	3,400
26-S	PDB	39.91	<20	<20	56	<20	<20	2,900
26-S	LF ⁺	39.16	<20	<20	<40	<20	<20	2,000
26-S ^R	LF ⁺	39.16	<1.0	<1.0	37	<1.0	<1.0	2,000

^RReplicate sample.

⁺Sample collected using submersible positive-displacement pump.

[#]Sample collected using peristaltic pump.



purge, and low-flow purge sample concentrations is caused by mixing of the stratified contamination or of areally heterogeneous concentrations during pumping.

A similar argument can be postulated to explain the substantial differences in concentration between the two methods at well 8-S during the first round of sampling (table 2). The resampling with multiple PDB samplers shows that concentrations shallower than 26 ft deep differ from those at 30 ft deep (fig. 3B). The TCE concentration in the low-flow sample is an approximate average of the concentrations measured across the length of the well screen with the PDB samplers. The 1,2-DCE concentration is higher in water from the low-flow sample than from the PDB sampler; however, this may be expected in an area where the 1,2-DCE concentration increased with depth from 110 to 640 $\mu\text{g/L}$ over an interval of 5 ft (fig. 3B). Because the low-flow sample was collected from the base of the interval, it is not unreasonable to suppose that concentrations continued to increase with depth below the sampled interval, and that the low-flow sample represents an integration of water that included higher concentrations than were evident from the PDB samplers. Thus, the data are again consistent with the hypothesis that the PDB samplers accurately reflected the ambient VOC concentrations.

Well 19-S is another well where discrepancies were noted between TCE concentrations from the conventional-purge samples and the PDB samples (table 2). Resampling the well by using multiple PDB samplers and low-flow sampling again showed substantial discrepancies in the TCE concentrations; however, examination of the vertical TCE-concentration distribution strongly suggests that the low-flow sample represents a mixing of stratified TCE layers in the screened interval (fig. 3C). The data again suggest that the PDB samplers provided an accurate representation of ambient concentrations. The difference in TCE concentrations measured between the two sampling events (410 to 610 $\mu\text{g/L}$ in November 1999 and 130 to 310 $\mu\text{g/L}$ in May 2000) is consistent with observation that TCE concentrations have shown substantial temporal variability in previous years (Keith Henn, Tetra Tech NUS, written commun., 2000).

Substantial discrepancies in the 1,2-DCE and TCE concentrations between the PDB sampling and the conventional sampling also were observed in water from well 3-S during the first test (table 2). A possible explanation for the poor agreement is that the diffusion sampler was not properly positioned. When the sampler was recovered, at least 5 ft of line that was intended to be below the water table was dry, implying that the diffusion sampler was inadvertently placed too shallow and possibly even partially above the water table. Thus, a comparison of the two approaches during the first test may be inappropriate. During the second test at the well, however, data from the PDB samplers showed that concentrations of 1,1,1-trichloroethane (1,1,1-TCA), 1,1-dichloroethane (1,1-DCA), 1,2-DCE, and TCE were stratified along the length of the well screen (fig. 3D, table 4). The data suggest that the low-flow sampling represents an averaging of concentrations, whereas the PDB sampler represents concentrations at points (fig. 3D).

In wells 8-D and 26-S, no substantial vertical concentration stratification was observed (figs. 3E, 3F), despite the substantial difference in concentrations obtained by the PDB samplers and the conventional purge sampling (table 2). When well 8-D was sampled by using low-flow purging, the concentrations from the pumped sample were similar to those in the PDB samplers (0.1- $\mu\text{g/L}$ difference for 1,1-DCA, 3- $\mu\text{g/L}$ difference for 1,2-DCE, 1.8- $\mu\text{g/L}$ difference for benzene, and 9- $\mu\text{g/L}$ difference for TCE) (table 4). The concentration discrepancy obtained while using the conventional purge approach probably was a reflection of pumping 260 gallons of water and may represent lateral mixing of chemically heterogeneous water. At well 26-S, TCE concentrations obtained by using the conventional purge approach were substantially higher than in water from the PDB sampler (table 2), and concentrations obtained by using low-flow sampling were substantially lower than those in water from the PDB sampler (fig. 3F). These data and the previous discussion suggest that the pumped sample integrated water with different concentrations than those that were present in the screened interval of the well.

SUMMARY

VOC concentrations from PDB samplers were compared to VOC concentrations from conventional purge sampling and low-flow purge sampling in side-by-side tests at NIROP, in Fridley, Minnesota. PDB samplers were tested in 19 wells at NIROP. The samplers were deployed in October 1999, allowed to equilibrate approximately 30 days, and recovered in November 1999. In a second test, PDB samplers were deployed in 7 wells in April 2000, allowed to equilibrate approximately 35 days, and recovered in May 2000.

A comparison of 1,2-DCE and TCE concentrations obtained by using PDB samplers and the conventional purge method in wells where one PDB sampler was deployed showed good agreement at several wells but poor agreement in others. For this investigation, good agreement was considered to be less than 5 µg/L difference for 1,2-DCE and less than 10 µg/L or less than 10 percent difference for TCE. Of the sites that did not meet these criteria, some sites (wells 3-IS and 9-S) had higher concentrations in water from the PDB sampler than in water from the conventional purge sample, implying that the PDB sampler more accurately reflected the local concentrations.

Concentration data from multiple diffusion samplers during the conventional-purge sampling and during the low-flow sampling indicates that the VOC concentrations in many of the wells are stratified within the screened interval. At well 18-S, TCE concentrations ranged from 470 to 1,600 µg/L over a vertical distance of approximately 6 ft. In this and other wells where stratification was observed, the concentration in the pumped sample appears to represent a mixing of waters having differing concentrations, whereas the PDB samplers represent localized concentrations. Other discrepancies between VOC concentrations from the conventional purge method and the PDB samplers appear to be related to the removal of multiple casing volumes of water (in some cases more than 100 gallons) prior to sampling. The data suggest that the VOC concentrations from the PDB samplers accurately reflect the VOC distribution in the screened interval of the tested wells. The data further suggest that PDB samplers are a viable method for sampling ground-water VOCs at NIROP. Multiple diffusion samplers may be required at some sites where contaminant stratification is present in the screened or open interval.

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Evaluation of a Diffusion Sampling Method for Determining
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USGS Water-Resources Investigations Report 00-4242

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By Peter E. Church

Abstract

Ground-water samples were collected in May 1999 at the Hanscom Air Force Base, Bedford, Massachusetts, with a method involving water diffusion samplers and a conventional low-flow sampling method to evaluate the use of diffusion samplers as an inexpensive and reliable alternative method for monitoring volatile organic compounds at the base. The principal compounds detected by both sampling methods were 1,2-dichloroethylene isomers, which ranged in concentration from not detected to nearly 7,000 micrograms per liter, and trichloroethylene, which ranged in concentration from not detected to nearly 5,000 micrograms per liter. A Sign test, applicable to these highly skewed concentrations, indicates that with a probability of 95 percent, it is equally likely to have diffusion sample concentrations of 1,2-dichloroethylene isomers and trichloroethylene greater than low-flow sample concentrations as it is to have diffusion sample concentrations of these compounds less than low-flow sample concentrations.

Analysis of the distribution of 1,2-dichloroethylene isomers and trichloroethylene concentrations in samples from long-screen wells (screen length 10 feet or greater) with multiple-diffusion samplers indicates that vertical concentration

variations within well screens differ substantially from sampled wells at the base. These concentration variations can be attributed to concentration stratification in the aquifer adjacent to the well screen; however, data from borehole-flowmeter logs from selected long-screen wells suggest that wellbore flow also may be a factor affecting concentration variations. Where water quality varies vertically along a well screen, water sampled with multiple diffusion samplers may better characterize water quality in the well than low-flow samples.

INTRODUCTION

Volatile organic compounds (VOCs) are present in ground water at Hanscom Air Force Base (AFB), Massachusetts. These VOCs include chlorinated solvents, petroleum hydrocarbons, and their biodegradation products. Remediation efforts to remove VOCs from ground water have been ongoing at the base since 1991. Considerable amounts of time and money are spent each year to collect water samples from monitoring wells using conventional low-flow techniques as part of a remediation-monitoring programs at sites such as this. An alternative, lower-cost sampling method that will save time and yield reliable results would be advantageous to all services and agencies involved in such activities.

Vroblesky and Hyde (1997) describe an inexpensive and effective sampling method that uses water-to-water polyethylene-membrane diffusion samplers (referred to as diffusion samplers in this report) placed in wells. Although this passive method has yielded promising results in some settings (Vroblesky and Hyde, 1997), additional testing is needed to evaluate its suitability as a long-term monitoring tool at Hanscom AFB. Also of concern at the base are the vertical distribution of VOCs in long-screen wells (screen length 10 ft or greater) and possible redistribution of VOCs caused by vertical flow in these wells.

The U.S. Geological Survey (USGS), in cooperation with the Air Force Center for Environmental Excellence (AFCEE), Brooks Air Force Base, San Antonio, Texas, and in consultation with the Restoration Program Manager at Hanscom AFB, designed a ground-water-sampling and borehole-logging program to compare VOC concentrations in water samples collected with the diffusion sampling method and a low-flow sampling method. To support interpretation of the water-quality data, multiple diffusion samplers were placed in long-screen wells and an open borehole in bedrock to examine the vertical distribution of VOC concentrations and to evaluate possible effects of flow in well screens on the vertical distribution of VOCs in selected wells.

The USGS installed diffusion samplers in wells during April 1999; samplers were retrieved in May 1999. The IT Corporation, Hopkinton, Mass., under contract to the Hanscom AFB, collected ground-water samples with the low-flow sampling method in May 1999, soon after retrieval of diffusion samplers. Vertical flow was measured by the USGS in four long-screen wells with a borehole flowmeter in June 1999.

The diffusion sampling method was chosen for testing as a possible alternative method over the current low-flow method used at the Hanscom AFB because diffusion samplers were expected to require less overall time for sampling, and lower costs for equipment and labor. Low-flow sampling methods, designed for collection of ground-water samples adjacent to well screens, while minimizing disturbance to the aquifer and drawdowns in the well casings (Puls and Barcelona, 1995), require purging the well-screen water until various water-quality parameters stabilize, collection and disposal of the purged water, and decontamination of the downhole sampling equipment before collection of a sample from another well. The diffusion sampling method eliminates the monitoring of water-quality

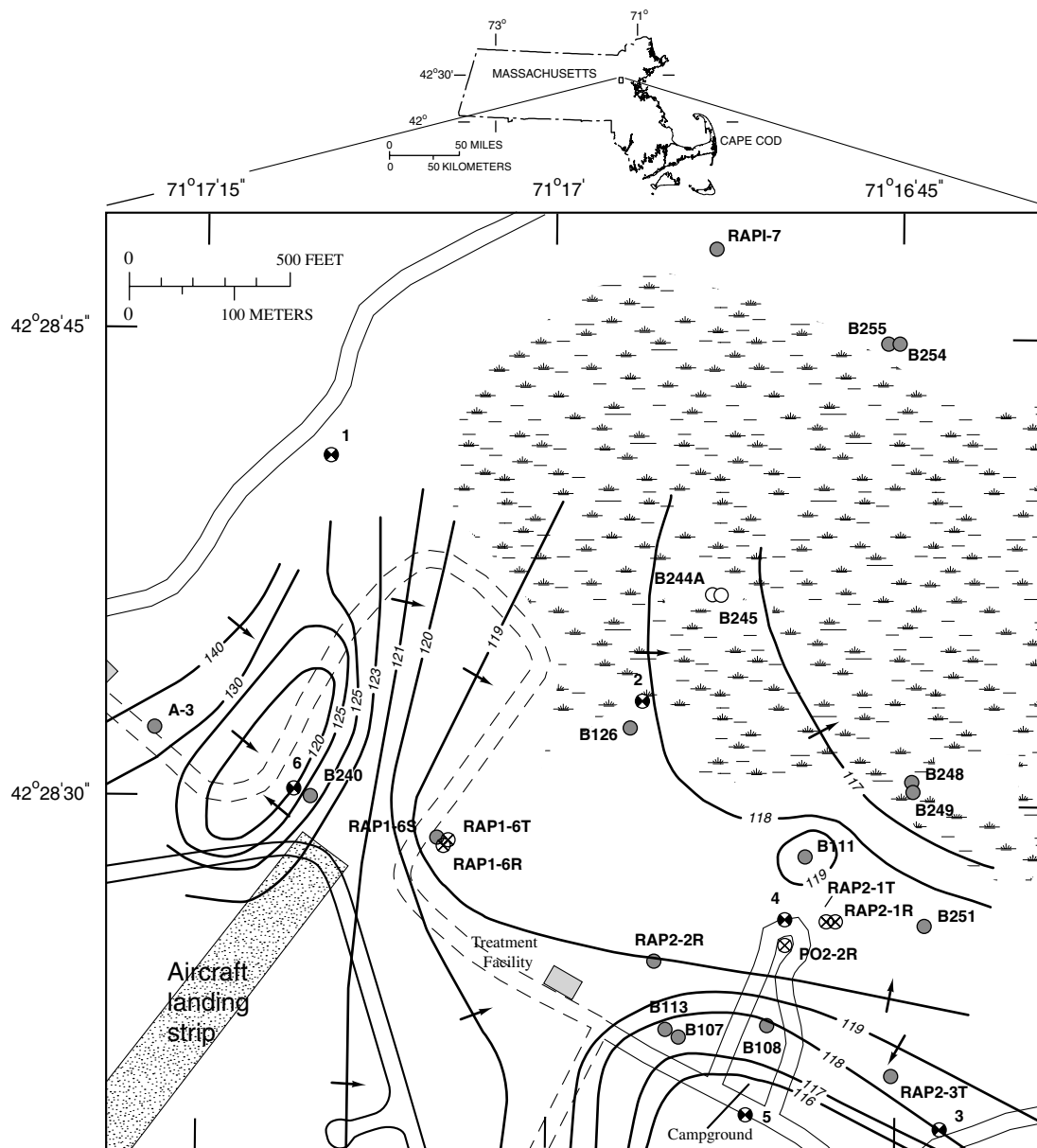
parameters and generates little to no waste water for disposal. Therefore, assuming that the quality of water in the well screen is representative of the water quality in the adjacent aquifer, the diffusion sampling method may prove to be a reliable alternative to the low-flow method.

This report compares a diffusion sampling method to a low-flow sampling method for monitoring of VOCs in ground water at the Hanscom AFB. The report also describes the possible effects of vertical variations of VOCs and borehole flow in long-screen wells on sampling with diffusion and low-flow methods.

The author thanks personnel of the Air Force Center for Environmental Excellence, Brooks AFB, San Antonio, Texas and Tom Best, Restoration Program Manager, Hanscom AFB, for their cooperation in developing the study program. Tom Best provided pertinent site information and assistance in the field, and personnel of IT Corporation, Hopkinton, Mass., collected the low-flow samples. The helpful comments throughout this study from Richard Willey, Office of Site Remediation and Restoration, U.S. Environmental Protection Agency, Region I, Boston, Mass., and the reviews of the report by Richard Willey and Javier Santillan, Air Force Center for Environmental Excellence, are greatly appreciated. William J. Andrade, Analytical Specialist and Joe Montanaro, Analyst, U.S. Environmental Protection Agency, Region I, Lexington, Mass., also are acknowledged for analyzing both the diffusion and low-flow samples and for providing guidance on quality-assurance procedures during the collection of water samples.

DESCRIPTION OF STUDY AREA

The study area is in the northeastern part of the Hanscom AFB in Bedford, Mass. (fig. 1). Physical, hydrogeological, and hydraulic characteristics of this area have been described by Haley & Aldrich, Inc. (1996, 1998). The land surface ranges in altitude from about 110 to 125 ft in most of the study area. In the west-central part of the study area, near well A-3, land-surface altitude increases to greater than 145 ft. Swamps occupy the north-central and eastern part of the study area. Surface drainage at the Hanscom AFB is controlled by storm culverts and swales that drain to the northwest, northeast, and east.



Base from the U.S. Geological Survey 7.5 x 15 minute quadrangle topographic map
Maynard, Massachusetts base map, 1:25,000, 1987
Based on Massachusetts coordinate system

EXPLANATION








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|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  SWAMP |  RAP1-6T WELLS SAMPLED BY WATER
DIFFUSION AND LOW-FLOW METHOD
AND IDENTIFIER; VERTICAL FLOW
MEASURED |
|  117 WATER-TABLE CONTOURS—Shows
altitude of water table in May 1998 (Haley
and Aldrich, Inc., 1998).
Contour interval is variable. Datum is
sea level. |  2 RESTORATION WELLS AND
IDENTIFIER |
|  B245 WELLS SAMPLED BY WATER
DIFFUSION METHOD AND
IDENTIFIER |  DIRECTION OF FLOW |
|  B249 WELLS SAMPLED BY WATER
DIFFUSION AND LOW-FLOW
METHOD AND IDENTIFIER | |

Figure 1. Location of study area, altitude of water table in May 1998, location of wells sampled with diffusion and low-flow sampling methods, wells logged with a borehole flowmeter, and restoration wells, Hanscom Air Force Base, Bedford, Massachusetts.

VOCs are present in surficial aquifers, a shallow aquifer that is unconfined, a deep confined aquifer, and the underlying fractured bedrock aquifer that also is confined. The shallow aquifer consists of fine sand and silt of glacial outwash deposits. The deep confined aquifer consists of a wide range of particle sizes from silt to boulders [previously described as glacial till by Haley & Aldrich, Inc. (1996), and hereafter referred to as till] below a confining layer of lacustrine silt. The bedrock is composed primarily of granitic gneiss and schists. The bedrock surface slopes from a depth of about 20 to 30 ft below land surface in the northern part of the study area to a depth of about 100 to 120 ft below land surface in the southern part of the study area. The outwash deposits at the surface range in thickness from about 8 to 28 ft and grade downward from silty, fine to medium sand to silty, fine to coarse sand. The lacustrine deposit ranges in thickness from less than 1 ft to about 48 ft and grades downward from fine sand and silt to clayey silt. Lacustrine sediments are not present in the west-central part of the study near well A-3 where the outwash is directly underlain by the sandy and gravelly till, which ranges in thickness from about 8 to 60 ft. In this report, the outwash deposits are referred to as the surficial aquifer, the confined till deposit as the till aquifer, and the fractured bedrock as the bedrock aquifer.

Water-level measurements in May 1998 (Haley & Aldrich, Inc., 1998) indicate that the water table within the study area ranged in altitude from about 116 to 140 ft (fig. 1). The water table is primarily in the surficial aquifer at depths of 0 to about 12 ft below land surface. Ground-water flow in the surficial aquifer is generally from the southwest to the northeast. In the west-central part of the site, where the lacustrine deposit is not present and the till is directly overlain by the outwash deposits, a cone of depression in the water table is formed by the continuous pumping of the bedrock aquifer by Restoration Well No. 6 (fig. 1). The water table in the southeastern part of the site appears to be affected by continuous pumping from Restoration Well No. 5 in the till aquifer. Pumping from Restoration Wells Nos. 1, 2, 3, and 4 (fig. 1) have formed a depression in potentiometric surfaces in the till and bedrock aquifers from the southeastern to the northwestern parts of the site (potentiometric surfaces in the till and bedrock aquifer are not shown

on fig. 1). Aquifer-test data from selected wells indicate horizontal hydraulic conductivities range from about 5 to 65 ft/d in the till aquifer and from about 0.1 to 0.6 ft/d in the bedrock aquifer (Haley & Aldrich, Inc., 1996).

SAMPLING METHODS

Water-quality samples were collected with the diffusion sampling method and a low-flow sampling method. Duplicate samples, and equipment and trip blank samples, were collected for each sampling method to assess the quality of the data collected. Vertical flow was measured in selected long-screen wells with a borehole flowmeter.

Diffusion Samplers

Diffusion samplers were constructed based on the method described by Vroblesky and Hyde (1997). Polyethylene sleeves, 2-inch wide by 18-inch long, and 4 mil thick, were heat sealed at one end, filled with about 300 mL of deionized water, and then closed by heat sealing the other end after the elimination of any air space. The water-filled polyethylene tubes were slid into 24-inch long, 1.5-inch diameter polyethylene-mesh tubing and secured to plastic-covered cords at both ends with plastic cable ties. The diffusion samplers then were lowered into wells with weights attached to the cords, either to depths within well screens or to an open borehole in bedrock. The depths were measured from the midpoint of the samplers to the top of the well casing. The samplers remained in the wells for about 3 weeks before recovery to allow time for VOCs diffusing into the samplers to equilibrate with VOCs in the aquifer.

Upon retrieval, the polyethylene mesh was partially cut open, a small slit was made at the top of a sampler, and the water samples were decanted into 40-milliliter glass vials. Hydrochloric acid (about 0.1 mL) was added to the vials to preserve the sample. Once capped, the vials were packed in ice. Samples were hand delivered to the nearby U.S. Environmental Protection Agency (USEPA) laboratory in Lexington,

Mass., at the end of each day for analysis of VOCs by USEPA method 8260 (U.S. Environmental Protection Agency, 1996).

Seventy diffusion samplers were placed in 23 wells on April 21 and 22, 1999. Fourteen of these wells had screens that were at least 10 ft long or longer and multiple diffusion samplers were placed in these wells. Five wells with 10-foot screens each contained three diffusion samplers; in each well, one sampler was placed about 1 ft above the bottom of the screen, one at the middle of the screen, and one about 1 ft below the top of the screen. Eight wells with screens longer than 10 ft each contained five diffusion samplers that were equally spaced from about 1 ft above the bottom of the screen to about 1 ft below the top of the screen. Five samplers also were placed in the open bedrock well; these were equally spaced as in the long-screen wells.

Each of the eight remaining wells, which had screens 10 ft long or shorter, contained a single diffusion sampler placed at the midpoint of the screen. In the case where the water level was below the top of the screen, the diffusion sampler was placed at the midpoint between the water level and the bottom of the screen. At well RAP1-6S, a long-screen well open to the water table, only two diffusion samplers were installed in the 6 ft of water within the 14.5-foot long screen.

Diffusion samplers were retrieved during May 10–13, 1999, generally in order of increasing VOC concentration as determined from results of previous sampling (Haley & Aldrich, Inc., 1998). The comparison between the diffusion and the low-flow sampling methods was made using the midpoint diffusion sampler in wells where multiple samplers were installed. Because a diffusion sampler was not placed at the midpoint between the water level and the bottom of the screen in well RAP1-6S, the depth at which the low-flow sample was obtained, concentrations from this well were not used in the comparison of diffusion and low-flow sampling method. Relevant diffusion sampling information are summarized in Church and Lyford (2000).

Low-Flow Sampling

A bladder pump was used by IT Corporation, Hopkinton, Mass., to collect water samples with the low-flow sampling method. The pump intake was placed at the midpoint of each well screen. In the case where the water level was below the top of the screen, the pump intake was placed at the midpoint between the water level and the bottom of the screen. Purge rates were adjusted from about 0.1 to 1.0 L/min (0.26 gal/min) according to the rate of inflow to each well to minimize drawdown. Drawdowns measured during sampling ranged from negligible to 1.42 ft, however, drawdowns in 86 percent of the wells sampled were less than 0.5 ft. Water-quality field parameters, water temperature, specific conductance, pH, and turbidity were monitored at 5-minute intervals, and a sample was collected after these field parameters stabilized. The stabilization criteria for these field parameters are: water temperature, ± 1 degree Celsius; specific conductance, ± 5 percent microsiemens per centimeter; pH, ± 0.1 pH unit; turbidity, ± 10 nephelometric units. Samples were processed and analyzed using the same procedures that were used with the diffusion samples.

Samples were collected from 21 wells with the low-flow sampling method May 10–14, 1999, after the diffusion samplers were retrieved. The wells B244A and B245, from which diffusion samples were obtained, were not sampled by the low-flow method because of the difficulty in transporting sampling equipment to these wetland locations. Low-flow water samples generally were collected within one day after the diffusion samples were collected and in the same order that the samplers were retrieved from the wells. Relevant low-flow sampling information are summarized in Church and Lyford (2000).

Borehole Flowmeter

Vertical flow in wells was measured using a borehole flowmeter, which consists of a downhole probe with heat sensors located equidistant above and below a heat source at the bottom of the probe (Keyes, 1990). The heat source is a thin metal mesh through which water flows. A pulse of electricity causes this mesh to increase in temperature, thereby increasing the temperature of a small parcel of water. Travel time of the heated water is measured as it passes either of the

heat sensors, and vertical direction is determined by the sensor that detected the heated water. The annular space between the probe's heat source and the well screen or casing must be sealed to direct vertical flow, if any, through the metal mesh. Travel times are calibrated to well diameter, and flow rates are expressed in gallons per minute. If the annular space between the heat source and the well screen has been properly sealed and the water-level changes caused by introducing the probe have stabilized, accuracies of ± 5 percent can be obtained for vertical-flow measurements under static conditions. The minimum flow rate that can be detected by the borehole flowmeter used at this site is reported as 0.03 gal/min by the manufacturer (Mount Sopris Instruments, Golden, Colo.). Field experience with this flowmeter indicates that flow rates as low as 0.01 gal/min can be detected before the measurement is affected by thermal convection (B.P. Hansen, U.S. Geological Survey, oral commun., 1999)

Borehole-flowmeter logging was conducted under ambient (unstressed) and pumping (stressed) conditions in five wells at the base; two screened in the till aquifer, two screened in bedrock aquifer, and one in the open borehole in bedrock aquifer. Reliable flowmeter measurements under unstressed conditions were not obtained from the two wells screened in bedrock because the water levels in the well casing had not stabilized 2 hours after water was displaced by lowering the logging probe. In the open borehole in bedrock, the annular space between the probe and the bedrock wall could not be sealed, and reliable data under unstressed and stressed conditions could not be obtained.

EVALUATION OF SAMPLING METHODS

The principal VOCs detected with both sampling methods were 1,2-dichloroethylene isomers (1,2-DCE) and trichloroethylene (TCE). Concentrations of 1,2-DCE in diffusion samples ranged from below the minimum reporting limit of 5 micrograms per liter ($\mu\text{g/L}$) to 6,800 $\mu\text{g/L}$ for 1,2-DCE and to 4,900 $\mu\text{g/L}$ for TCE. Concentrations in water samples collected with the low-flow method ranged from below the minimum reporting limit of 5 $\mu\text{g/L}$ to 6,400 $\mu\text{g/L}$ for 1,2-DCE and 4,900 $\mu\text{g/L}$ for TCE (table 1). Other VOCs detected, but generally at lower concentrations, include

acetone, vinyl chloride, 1,1-dichloroethylene (1,1-DCE), and 1,1-dichloroethane (1,1-DCA) (Church and Lyford, 2000).

Samples were collected at the midpoint of well screens (and at the midpoint of the open hole in bedrock) in 20 wells with both methods. Because VOCs were not detected in all wells, and many of the VOCs detected had concentrations outside of the calibration ranges of analytical instruments, the number of wells with paired samples for comparison of sampling methods was reduced to 10 for concentration of 1,2-DCE and 16 for concentration of TCE (table 2, figs. 2 and 3). Concentrations of vinyl chloride were detected within analytical instrument calibration ranges in samples at the midpoint of well screens with both methods from only two wells, and 1,1-DCA from only one well. Acetone, commonly detected in laboratory blank samples (Church and Lyford, 2000), and 1,1-DCE were not detected in any samples from the midpoint of well screens with either sampling method. Therefore, only 1,2-DCE and TCE concentrations are used to evaluate the diffusion sampling method as an alternative to the low-flow sampling method. Concentrations of 1,2-DCE used in this comparison of methods ranged from 8.2 to 2,500 $\mu\text{g/L}$ in diffusion samples and 5.9 to 2,600 $\mu\text{g/L}$ in low-flow samples. Concentrations of TCE ranged from 12 to 4,900 $\mu\text{g/L}$ in diffusion samples and 11 to 4,900 $\mu\text{g/L}$ in low-flow samples (table 2).

Quality Assurance for Sampling Methods

Quality assurance for water samples collected with diffusion samplers included an equipment blank, daily trip blanks, and duplicate samples for about 7 percent of the samples collected. The equipment blank was the deionized water contained in a diffusion sampler exposed to air for about one week. Quality assurance for water samples collected with low-flow method included daily equipment blanks, a trip blank, and duplicate samples for about 14 percent of the samples. The USEPA Laboratory quality-assurance procedures included matrix spike samples made from selected diffusion samples and low-flow samples, and lab blanks (Church and Lyford, 2000).

Table 1. Concentrations of volatile organic compounds in ground-water samples collected with diffusion and low-flow sampling methods from wells at Hanscom Air Force Base, Bedford, Massachusetts, May 10–14, 1999

[Blank spaces indicate that only one low-flow sample was collected per well; samples were not collected from wells B244A and B245 with the low-flow sampling method. B, analyte found in lab blank; E, estimated value exceeds calibration range; L, estimated value is below calibration range; µg/L, micrograms per liter; --(5), not detected at reporting limit of 5 µg/L]

Well name	Water diffusion sampler name	Diffusion sampler depth, in feet below land surface	Low-flow sample depth, in feet below land surface	1,2-Dichloroethylene isomers (µg/L)		Trichloroethylene (µg/L)	
				Diffusion sample	Low-flow sample	Diffusion sample	Low-flow sample
A-3	A-3	48.0	48.0	--(5)	--(5)	--(5)	--(5)
RAP1-6S	RAP1-6S-A	8.1	11.0	37	12	9.2	2.8(L)
RAP1-6S	RAP1-6S-B	12.1		59		16	
B107	B107	13.3	13.5	--(5)	--(5)	--(5)	--(5)
B255	B255	99.5	99.5	--(5)	--(5)	--(5)	--(5)
B254	B254	64.5	64.5	1.4(L)	--(5)	7.6	2.6(L)
RAP1-7	RAP1-7-A	39.0		5.1		56	
RAP1-7	RAP1-7-B	44.75		--(100)		280	
RAP1-7	RAP1-7-C	50.5	50.5	--(50)	8.2(L)	180	180
RAP1-7	RAP1-7-D	56.25		--(50)		220	
RAP1-7	RAP1-7-E	62.0		9.7(L)		190	
B126	B126-A	52.7		8.4		15	
B126	B126-B	56.7	56.5	14	11	22	19
B126	B126-C	60.7		11		20	
B111	B111-A	58.0		7.8		65	
B111	B111-B	61.8	62.0	8.2	5.9	85	47
B111	B111-C	65.6		9.1		77	
B244A	B244A-A	42.0		63		8.1	
B244A	B244A-B	46.5		65		5	
B244A	B244A-C	51.0		55		47	
B244A	B244A-D	55.5		61		46	
B244A	B244A-E	60.0		82		19	

Table 1. Concentrations of volatile organic compounds in ground-water samples collected with diffusion and low-flow sampling methods from wells at Hanscom Air Force Base, Bedford, Massachusetts, May 10–14, 1999 —*Continued*

Well name	Water diffusion sampler name	Diffusion sampler depth, in feet below land surface	Low-flow sample depth, in feet below land surface	1,2-Dichloroethylene isomers (µg/L)		Trichloroethylene (µg/L)	
				Diffusion sample	Low-flow sample	Diffusion sample	Low-flow sample
B245	B245	17.5		15		7.4	
B251	B251	72.5	72.5	1(L)	4.3(L)	18	22
B249	B249	95.0	95.0	2.9(L)	--(5)	35	18
B248	B248	59.5	59.5	170	130	470	260
B113	B113-A	54.7		98		32	
B113	B113-B	58.7	58.5	100	51	30	11
B113	B113-C	62.7		99		34	
PO2-2R	PO2-2R-A	103.5		10		43	
PO2-2R	PO2-2R-B	110.5		12		48	
PO2-2R	PO2-2R-C	117.5	117.5	16	25	56	68
PO2-2R	PO2-2R-D	124.5		140		350	
PO2-2R	PO2-2R-E	131.0		140		320	
RAP2-3T	RAP2-3T-A	67.6		170		160	
RAP2-3T	RAP2-3T-B	70.8		14(L)		86	
RAP2-3T	RAP2-3T-C	74.0	74.0	35	77	200	170
RAP2-3T	RAP2-3T-D	77.2		28		160	
RAP2-3T	RAP2-3T-E	80.4		13(L)		71	
B108	B108-A	69.0		22		21	
B108	B108-B	73.0	73.0	25	7.4	12	16
B108	B108-C	77.0		26		14	
RAP2-1R	RAP2-1R-A	107.0		340		840	
RAP2-1R	RAP2-1R-B	110.5		300		890	
RAP2-1R	RAP2-1R-C	114.1	114.1	270	470	780	750
RAP2-1R	RAP2-1R-D	117.7		280		540	
RAP2-1R	RAP2-1R-E	121.2		260		490	
RAP2-1T	RAP2-1T-A	59.3		--(25)		55	
RAP2-1T	RAP2-1T-B	63.5		15(L)		230	
RAP2-1T	RAP2-1T-C	67.7	67.5	95	--(250)	900	880
RAP2-1T	RAP2-1T-D	71.8		82		1300	
RAP2-1T	RAP2-1T-E	76.0		97		990	

Table 1. Concentrations of volatile organic compounds in ground-water samples collected with diffusion and low-flow sampling methods from wells at Hanscom Air Force Base, Bedford, Massachusetts, May 10–14, 1999 —*Continued*

Well name	Water diffusion sampler name	Diffusion sampler depth, in feet below land surface	Low-flow sample depth, in feet below land surface	1,2-Dichloroethylene isomers (µg/L)		Trichloroethylene (µg/L)	
				Diffusion sample	Low-flow sample	Diffusion sample	Low-flow sample
RAP2-2R	RAP2-2R-A	82.9		1400		320	
RAP2-2R	RAP2-2R-B	87.5		1800		300	
RAP2-2R	RAP2-2R-C	92.0	92.0	1800	2,200	280	190
RAP2-2R	RAP2-2R-D	96.2		1800		270	
RAP2-2R	RAP2-2R-E	101.2		1900		350	
RAP1-6T	RAP1-6T-A	30.6		2400		410	
RAP1-6T	RAP1-6T-B	33.9		6800		1600	
RAP1-6T	RAP1-6T-C	37.0	37.0	6800(E)	6,200(E)	1600	1,500
RAP1-6T	RAP1-6T-D	40.4		6600(E)		1800	
RAP1-6T	RAP1-6T-E	43.7		6200(E)		1600	
RAP1-6R	RAP1-6R-A	52.5		5100(E)		1000	
RAP1-6R	RAP1-6R-B	57.0		5400(E)		1100	
RAP1-6R	RAP1-6R-C	61.6	61.5	6400(E)	6,400(E)	1400	1,200
RAP1-6R	RAP1-6R-D	66.2		6300(E)		1300	
RAP1-6R	RAP1-6R-E	70.7		5400		1100	
B240	B240-A	57.0		2200(B)		4400	
B240	B240-B	61.0	61.0	2500	2,600	4900	4,900
B240	B240-C	65.0		2500		4600	

Table 2. Concentrations, differences in concentrations, and estimated error in concentrations due to sampling and analytical processes of volatile organic compounds in ground-water samples collected with diffusion and low-flow sampling methods at Hanscom Air Force Base, Bedford, Massachusetts, May 10–14, 1999

[Comparison of range or error between sampling methods: >, range of error in diffusion sample is greater than the range of error in the low-flow sample; =, range of error in diffusion sample overlaps range of error in low-flow samples; <, range of error in diffusion sample is less than range of error in low-flow sample. Wells are listed in order of increasing low-flow sample concentration. µg/L, micrograms per liter]

Well	Concentration			Relative percent difference (RPD)	Concentration				Comparison of range of error between sampling methods
	Diffusion sample	Low-flow sample	Diffusion sample minus low-flow sample		Range of error due to sampling and analytical processes (±10 percent)				
					Diffusion sample		Low-flow sample		
					Low	High	Low	High	
1,2-dichloroethylene isomers (µg/L)									
B111	8.2	5.9	2.3	33	7.38	9.02	5.31	6.49	>
B108	25	7.4	17.6	109	22.5	27.5	6.66	8.14	>
B126	14	11	3	24	12.6	15.4	9.9	12.1	>
PO2-2R	16	25	-9	44	14.4	17.6	22.5	27.5	<
B113	100	51	49	65	90	110	45.9	56.1	>
RAP2-3T	35	77	-42	75	31.5	38.5	69.3	84.7	<
B248	170	130	40	27	153	187	117	143	>
RAP2-1R	270	470	-200	54	243	297	423	517	<
RAP2-2R	1,800	2,200	-400	20	1,620	1,980	1,980	2,420	<
B240	2,500	2,600	-100	4	2,250	2,750	2,340	2,860	=
Average.....				45					
Trichloroethylene (µg/L)									
B113	30	11	19	93	27	33	9.9	12.1	>
B108	12	16	-4	29	10.8	13.2	14.4	17.6	<
B249	35	18	17	64	31.5	38.5	16.2	19.8	>
B126	22	19	3	15	19.8	24.2	17.1	20.9	=
B251	18	22	-4	20	16.2	19.8	19.8	24.2	<
B111	85	47	38	58	76.5	93.5	42.3	51.7	>
PO2-2R	56	68	-12	19	50.4	61.6	61.2	74.8	=
RAP2-3T	200	170	30	16	180	220	153	187	=
RAP1-7	180	180	0	0	162	198	162	198	=
RAP2-2R	280	190	90	38	252	308	171	209	>
B248	470	260	210	58	423	517	234	286	>
RAP2-1R	780	750	30	4	702	858	675	825	=
RAP2-1T	900	880	20	2	810	990	792	968	=
RAP1-6R	1,400	1,200	200	15	1,260	1,540	1,080	1,320	=
RAP1-6T	1,600	1,500	100	6	1,440	1,760	1,350	1,650	=
B240	4,900	4,900	0	0	4,410	5,390	4,410	5,390	=
Average.....				27					

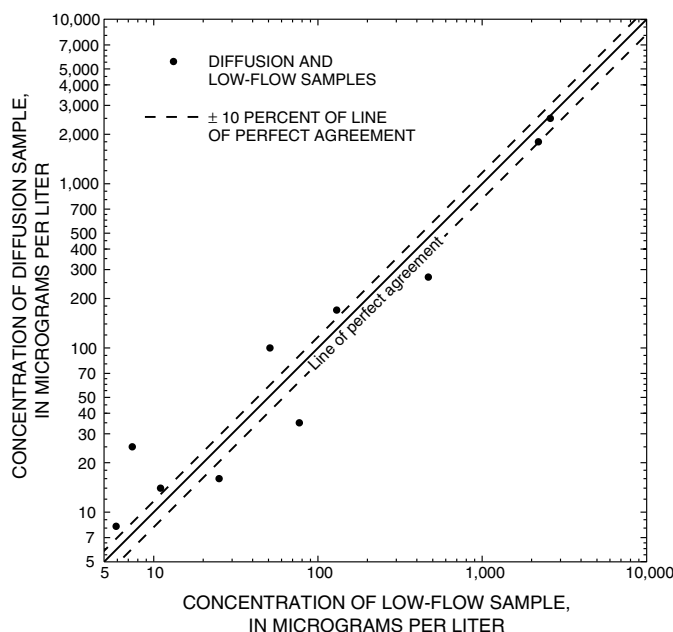


Figure 2. Comparison of 1,2-dichloroethylene isomers in ground water collected with diffusion and low-flow sampling methods, Hanscom Air Force Base, Bedford, Massachusetts, May 1999.

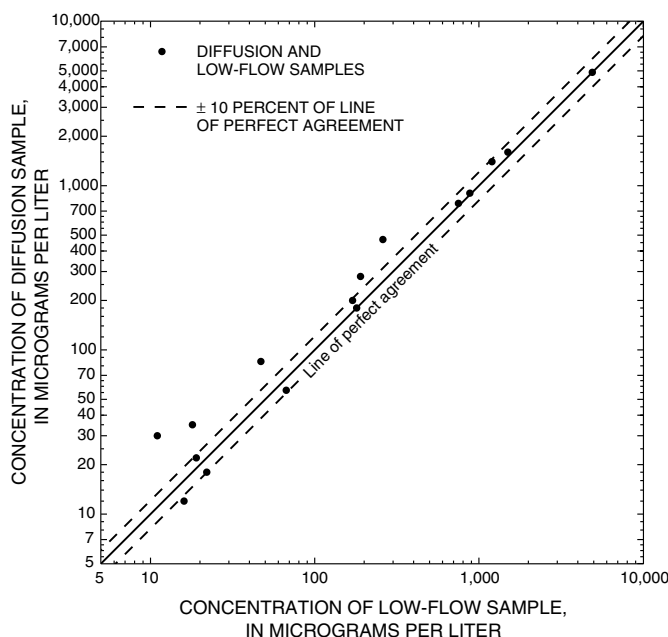


Figure 3. Comparison of trichloroethylene in ground water collected with diffusion and low-flow sampling methods, Hanscom Air Force Base, Bedford, Massachusetts, May 1999.

The VOCs 1,2-DCE and TCE were not detected above reporting limits in the diffusion and low-flow trip blank samples. They also were not detected above reporting limits in the diffusion sampling equipment blank sample and in most of the low-flow sampling equipment blank samples. Concentrations of 1,2-DCE (12 µg/L) and TCE (56 µg/L) were detected in the low-flow equipment blank sample on the last day of sampling when wells with the highest 1,2-DCE and TCE concentrations were sampled. Assuming the equipment blank concentrations were derived from the first well sampled on this day (RAP2-2R), concentrations of the second sample collected, and perhaps the two additional samples collected on this day, may be affected by contamination of the low-flow sampling equipment. In this case, the 1,2-DCE concentration of the equipment blank would be about 0.2 percent of the concentrations in the low-flow samples from wells RAP1-6T and RAP1-6R (6,200 µg/L and 6,400 µg/L), and about 0.5 percent of the concentration in the sample from well B240 (2,600 µg/L). Although the 1,2-DCE concentrations in samples from wells RAP1-6T and RAP1-6R exceed the calibration range of the analytical instrument, and as such are qualitative estimates, they demonstrate, as does the concentration in the sample from well B240, that the contaminated equipment blank has minimal effect on the 1,2-DCE concentrations in samples from these wells. The TCE concentration of the equipment blank, however, may account for about 4 percent of the TCE concentration in the sample from well RAP1-6T (1,500 µg/L), 5 percent of the sample from well RAP1-6R (1,200 µg/L), and 1 percent of the sample well B240 (4,900 µg/L).

Thirteen laboratory blank samples were analyzed during the period that diffusion and low-flow samples were analyzed. The VOCs 1,2-DCE and TCE, as well as vinyl chloride, 1,1-DCA, and 1,1-DCE, were not detected in any of the laboratory blank samples.

Duplicate samples for 1,2-DCE and TCE concentrations were obtained with the diffusion sampling method in four wells (B111, B113, RAP2-1R, and RAP1-6R) that also were sampled with the low-flow method. Concentrations of 1,2-DCE in the original and duplicate samples in well RAP1-6R were reported as estimated values because the concentrations exceeded

the calibration range of analytical instrument. Concentrations 1,2-DCE from this well, therefore, are not included in the duplicate sample analysis for 1,2-DCE, nor in any other quantitative analyses. Relative percent differences (RPDs) in 1,2-DCE concentrations between the original and duplicate samples from the three remaining wells ranged from 7.7 to 8.3 percent, with an average of 8.1 percent. Concentration of 1,2-DCE in two of these duplicate samples are less than the concentrations in the original samples, and one is greater. RPDs for the original and duplicate sample concentrations of TCE from the four wells ranged from 1.2 to 15.4 percent, with an average of 6.1 percent. The RPD of 15.4 percent (from well RAP1-6R) appears anomalous compared to the other three RPDs, which ranged from 1.2 to 6.5 percent with an average of 3 percent. Concentration of TCE in two of these duplicate samples are less than those in the original samples, and two are greater. There appears to be no positive or negative bias in duplicate sample concentrations sampled with the diffusion method.

Duplicate samples were obtained with the low-flow sampling method in three wells (B254, B240, and RAP1-6R). Concentrations of 1,2-DCE in the original and duplicate samples from well RAP1-6R exceeded the calibration range, concentrations of 1,2-DCE in well B254 were not detected in original and duplicate samples, and concentrations of TCE in well B254 were estimated below the calibration range. As a result, low-flow duplicate sample analysis of 1,2-DCE concentrations is represented by samples from one well (B240), and in this case, the original and duplicate sample concentrations are the same (2,600 µg/L). TCE duplicate analysis is represented by concentrations from two wells (B240 and RAP1-6R); RPDs are 2.1 and 8.0 percent, with an average of about 5 percent. Concentration of TCE in one duplicate sample is less than that in the original sample, and TCE concentrations in the other duplicate sample is greater than that in the original sample.

The error in sample concentrations attributable to sampling methods and analytical processes is estimated as within ± 10 percent for both sampling methods, based on analyses of trip, equipment, and laboratory blank samples and duplicate samples. Concentrations of TCE in low-flow samples from wells RAP1-6T, RAP1-6R, and B240, however, contain additional

error, as much as 5 percent, due to the TCE detected in the equipment blank sample that represents the day that samples were collected from these wells.

Comparison of Concentrations of 1,2-DCE and TCE in Diffusion and Low-flow Samples

Concentrations of 1,2-DCE and TCE in samples collected with diffusion and low-flow methods, differences in concentrations, relative percent differences in concentrations, and ranges of error due to sampling and analytical processes are provided in table 2. These data show a wide range of concentrations, and a wide range of differences in concentrations of 1,2-DCE and TCE sampled with the diffusion and low-flow methods. Average RPD for 1,2-DCE concentrations from samples collected with both methods is about 45 percent, whereas the average RPD for TCE concentrations is about 27 percent (table 2), indicating substantially smaller differences between TCE concentration from diffusion and low-flow samples than differences between 1,2-DCE concentrations from both methods. With the estimated error attributable to sampling and analytical processes of ± 10 percent applied to each sample, and sample concentrations from both methods are considered to be the same if their ranges of error overlap, concentrations of 1,2-DCE in diffusion samples are greater than those in low-flow samples in 5 wells, are the same in one well, and are less in 4 wells. TCE concentrations in diffusion samples are greater than those low-flow samples in 5 wells, are the same in 9 wells, and are less in 2 wells (table 2).

Because the 1,2-DCE and TCE concentrations determined from both methods are highly skewed, even with a log₁₀ transformation, a Sign test, a non-parametric statistical test that can be applied to paired, non-normally distributed data sets with non-normally distributed differences (Helsel and Hirsch, 1992), was used to compare the concentrations from each method. The concentration data applied to this test include the estimated error of ± 10 percent for each diffusion and low-flow sample. Results of these statistical tests indicate, at a probability of 95 percent, that it is equally likely to have diffusion sample concentrations of 1,2-DCE and TCE greater than low-flow sample

concentrations as it is to have diffusion sample concentrations of 1,2-DCE and TCE less than low-flow sample concentrations. Therefore, results from evaluation of the diffusion sampling method indicate that use of diffusion samplers for collection of VOCs containing 1,2-DCE and TCE, and thus other VOCs, may be a viable alternative to the low-flow sampling method currently being used at this base.

It is useful to note, however, that the highest concentrations of 1,2-DCE and TCE in long-screen wells, which were determined from samples collected with multiple diffusion samplers placed in these wells, are not necessarily at the midpoint of well screens where low-flow samples were obtained (table 1). A non-midpoint sample concentration is considered to be higher than the midpoint sample concentration if the ranges of uncertainty (± 10 percent) in concentrations for each sample do not overlap. The highest concentrations of 1,2-DCE were detected in diffusion samples either above or below the midpoint sample in 36 percent of the long-screen wells. The highest concentrations of TCE were detected in samples either above or below the midpoint sample in 43 percent of the long-screen wells. This result demonstrates that, if the goal is to determine the highest concentrations of VOCs in a long-screen well, even if only to select where along the well screen a sample should be collected with another sampling method, use of diffusion samplers can be very effective in monitoring, or assisting in monitoring of VOCs in ground water.

DISTRIBUTION OF VOLATILE ORGANIC COMPOUNDS IN LONG-SCREEN WELLS

Analysis of concentrations of water samples obtained with multiple diffusion samplers in long-screen wells (screen length 10 ft or greater) indicate that vertical variations of concentrations of 1,2-DCE and TCE within well screens differ considerably in samples from well to well at this site. Because concentrations of 1,2-DCE and TCE also range widely at this site, standard deviations of 1,2-DCE and TCE concentrations within each well, normalized by their respective average concentrations, were calculated as indicators of the relative variations of concentrations among these wells. These normalized standard deviations

(NSDs) are shown in figure 4, ordered first by aquifer, second by increasing screen length, and third by increasing NSD for TCE concentrations. A low NSD indicates a small variation in concentrations in a well screen. An NSD was not calculated for 1,2-DCE concentrations in wells RAP2-3T, RAP2-1T, and RAP1-7 because 1,2-DCE was not detected above reporting limits in some of the diffusion samples in these wells.

Comparison between NSDs in these wells suggests increasing variations in concentrations of 1,2-DCE and TCE with increasing screen length (fig. 4). Vertical variations in concentrations among well screens of similar screen length and similar variations in concentrations within well screens of different length, however, also are apparent. The variations of 1,2-DCE and TCE concentrations in these wells may reflect the distribution of these concentrations in the aquifer adjacent to the wells. Wellbore flow also may have an appreciable effect on the distribution of contaminant concentrations in the long-screen wells at this site. Explanations of these variations in 1,2-DCE and TCE concentrations are discussed below for wells from which borehole-flowmeter data were obtained.

Till Aquifer

At well RAP1-6T (15.1 ft screen), 1,2-DCE and TCE concentrations in the upper diffusion sample are appreciably less than those in lower four samples (1,2-DCE concentrations in the bottom three samples are estimated above calibration range) (fig. 5). This difference in concentrations is likely due to the upper part of the screens placed in the fine-grained lacustrine deposit. Borehole-flowmeter data under unstressed conditions indicate a uniform upward flow of about 0.025 gal/min within the till, and then decreases to less than 0.01 gal/min in the overlying lacustrine deposit (fig. 5). Under pumping conditions, borehole flowmeter data indicate that most of the water pumped to the surface is from the lower third of the well screen (near the middle of the till deposit) and that little, if any, flow is contributed from the lacustrine deposit. The flowmeter data are consistent with the lithologic data in indicating that the till is more hydraulically conductive than the overlying lacustrine deposit.

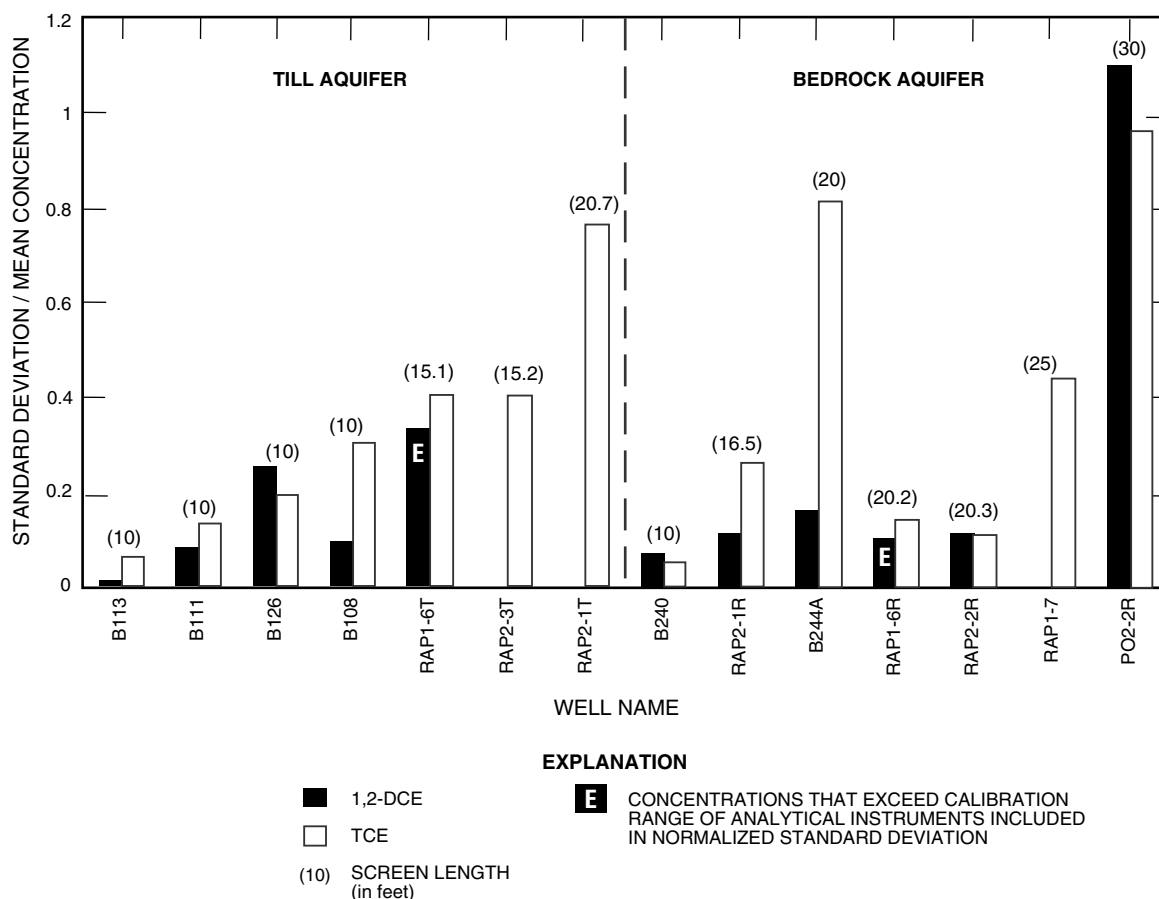


Figure 4. Normalized standard deviations of variations of 1,2-dichloroethylene isomers (1,2-DCE) and trichloroethylene (TCE) concentrations from multiple diffusion samples in long-screen wells, Hanscom Air Force Base, Bedford, Massachusetts.

Although the apparent uniform distribution of VOC concentrations with depth in the till also may be similar in the aquifer, it also is likely due to the upward unstressed flow in the well homogenizing the concentration in the part of the well screened in the till (fig. 5). The lower concentrations observed in the well screen opposite the lacustrine deposit probably indicates that most of the upward moving waters containing VOCs exit the well screen below the lacustrine deposit.

Concentrations of TCE in the midpoint diffusion sample and the low-flow samples are similar (fig. 5). The relative percent differences of these concentrations resulting from application of both methods are about 6 percent. These similar concentrations suggest that the same waters are sampled with both methods, but the source of water, whether from the aquifer adjacent to the sampling devices in the screen or from lower in the aquifer because of wellbore flow, is uncertain.

The vertical distribution of TCE concentrations at well RAP2-1T (fig. 6), where the upper 4 ft of the 20.7-foot well screen is in the lacustrine deposit, are similar to those observed at well RAP1-6T. Concentrations of TCE in the bottom four diffusion samples, where the well screen is in the till, are substantially higher than in the upper sample where the well is screened in the lacustrine deposit. Borehole flowmeter data indicate downward flow in the till under non-pumping (unstressed) conditions with a maximum flow of about 0.06 gal/min near the middle of the screen (fig. 6), indicating that the horizontal hydraulic conductivity of the till may be higher in this zone than in the overlying and underlying till. Although measurements of flow under unstressed conditions were not made in the upper part of the screen in the lacustrine deposit, the first measurement in the till, near the contact with the lacustrine deposit, was about 0.01 gal/min, indicating that little to no flow occurred in the lacustrine

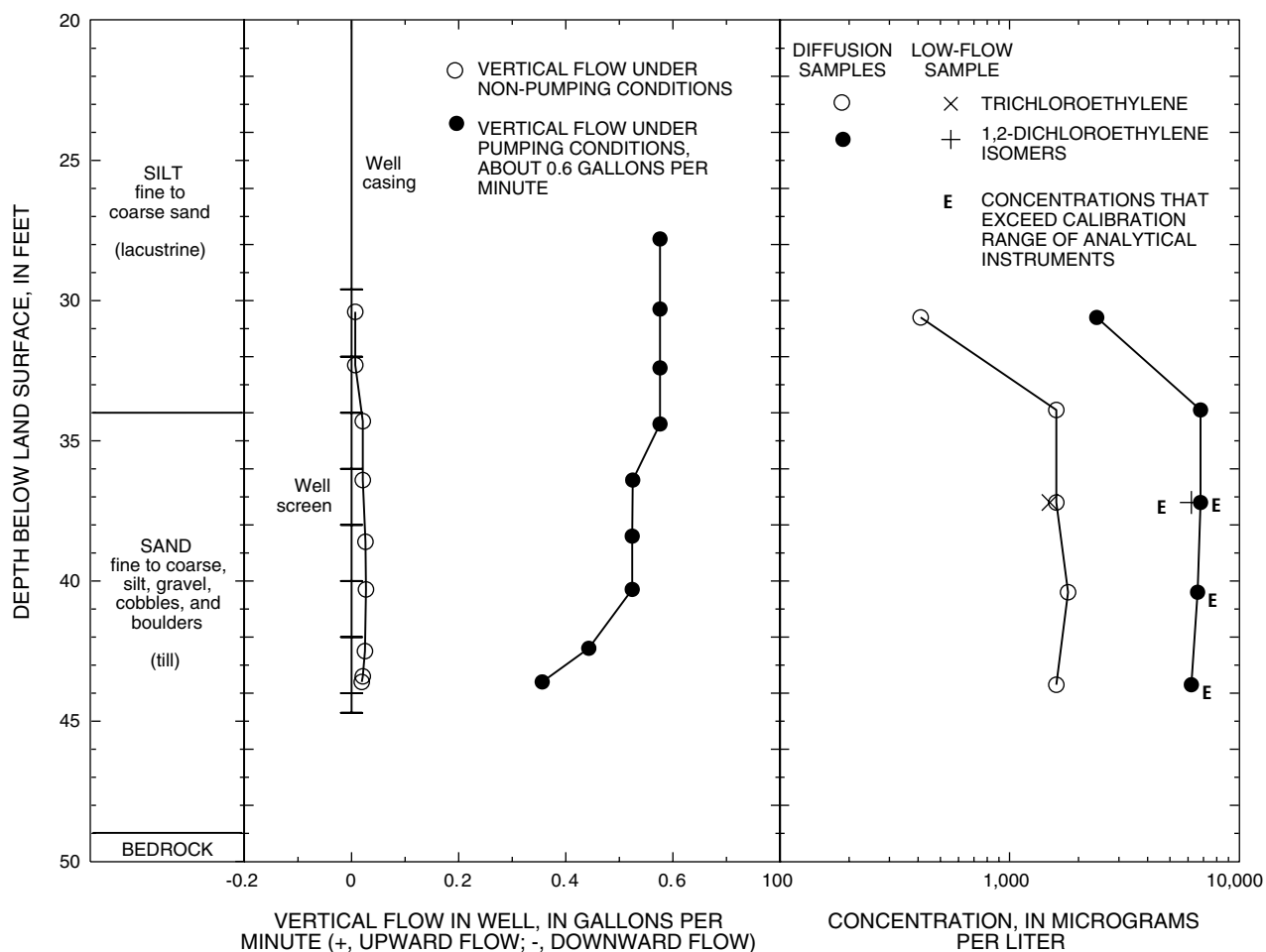


Figure 5. Lithology, well casing and screen, borehole-flowmeter data, and concentrations of 1,2-dichloroethylene isomers and trichloroethylene in multiple diffusion samples and in the low-flow sample at well RAP1-6T in the till aquifer at Hanscom Air Force Base, Bedford, Massachusetts.

deposit. Flow under pumping (stressed) conditions exhibits a nearly uniform increase in volume of water contributed to the well with decreasing depth in the till. The flow rate measured at the top of the till approximates the rate at which water was being pumped from the well, indicating that very little water, if any, was contributed from the lacustrine deposit.

The flowmeter data from this well are consistent with the lithologic data that indicate the point of contact between the lacustrine and till deposits. The unstressed flow data suggest that contaminants would flow preferentially within a zone near the middle of the part of the well screened in the till. Therefore, the relatively uniform TCE concentrations observed below this zone probably reflect the downward flow in the well screen. As in well RAP1-6T, the relatively lower concentration of TCE measured in the lacustrine deposit

could be the result of lower concentrations in this unit or insufficient time for the well water to equilibrate with the aquifer water after installing the diffusion samplers in the slower moving water of the lacustrine deposit.

The concentrations of TCE from the midpoint diffusion sample and the low-flow sample show little variation (fig. 6). The relative difference is about 2 percent. Because different dilution factors were used in these analyses, concentrations of 1,2-DCE were detected above the reporting limit of 25 µg/L in the diffusion sample and was not detected above the reporting limit of 250 µg/L in the low-flow sample (fig. 6), and, therefore, cannot be compared directly. The close correlation between TCE concentrations from both methods suggests that waters from the same source are being sampled, and flowmeter data suggest that much

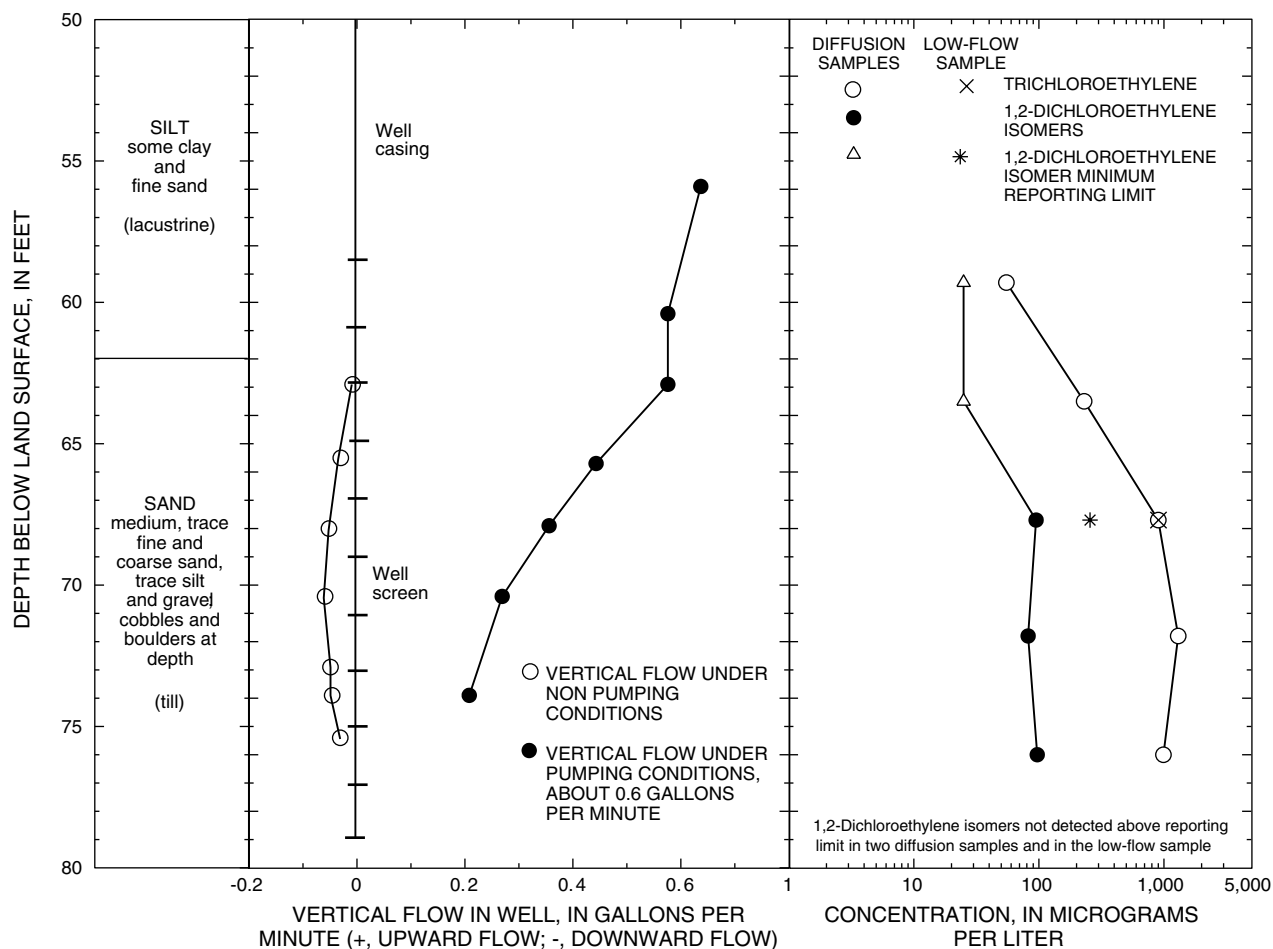


Figure 6. Lithology, well casing and screen, borehole-flowmeter data, and concentrations of 1,2-dichloroethylene isomers and trichloroethylene in multiple diffusion samples and in the low-flow sample at well RAP2-1T in the till aquifer at Hanscom Air Force Base, Bedford, Massachusetts.

of this water is from the aquifer adjacent to a midpoint zone in the screen. Downward flow in the screen of lower concentration water from the upper part of the till aquifer, and possibly from the lacustrine deposit, however, could dilute concentrations in water in the mid-section of the screen, and result in lower concentrations than in the adjacent aquifer.

Bedrock Aquifer

Variations in concentrations of 1,2-DCE and TCE at well RAP1-6R (20.2-ft well screen) are relatively small (fig. 7) (1,2-DCE concentrations in the upper four samples are estimated above calibration range) and are comparable to those in 10-foot screens in the till. Unstressed flow was not measured in this

well because the water level in the well casing had not stabilized after 2 hours since placing the flowmeter probe in the well. Vertical flow in the well screen, however, is suggested as a possible cause for the nearly uniform distribution of 1,2-DCE and TCE concentrations. Borehole flowmeter data under pumping conditions indicate that most of the water pumped was contributed from the bottom 6 ft of the screen; especially from a thin zone about 4 to 6 ft from the bottom (fig. 7). This contribution would be consistent with a fracture, or fracture zone in the bedrock in this vicinity. Although the driller's log describes the bedrock as highly fractured, the flowmeter data indicate that the only substantial water-bearing fractures are near the bottom of the well screen. The nearly uniform distribution of concentrations with depth in the well screen could be the result of downward flow of contaminants

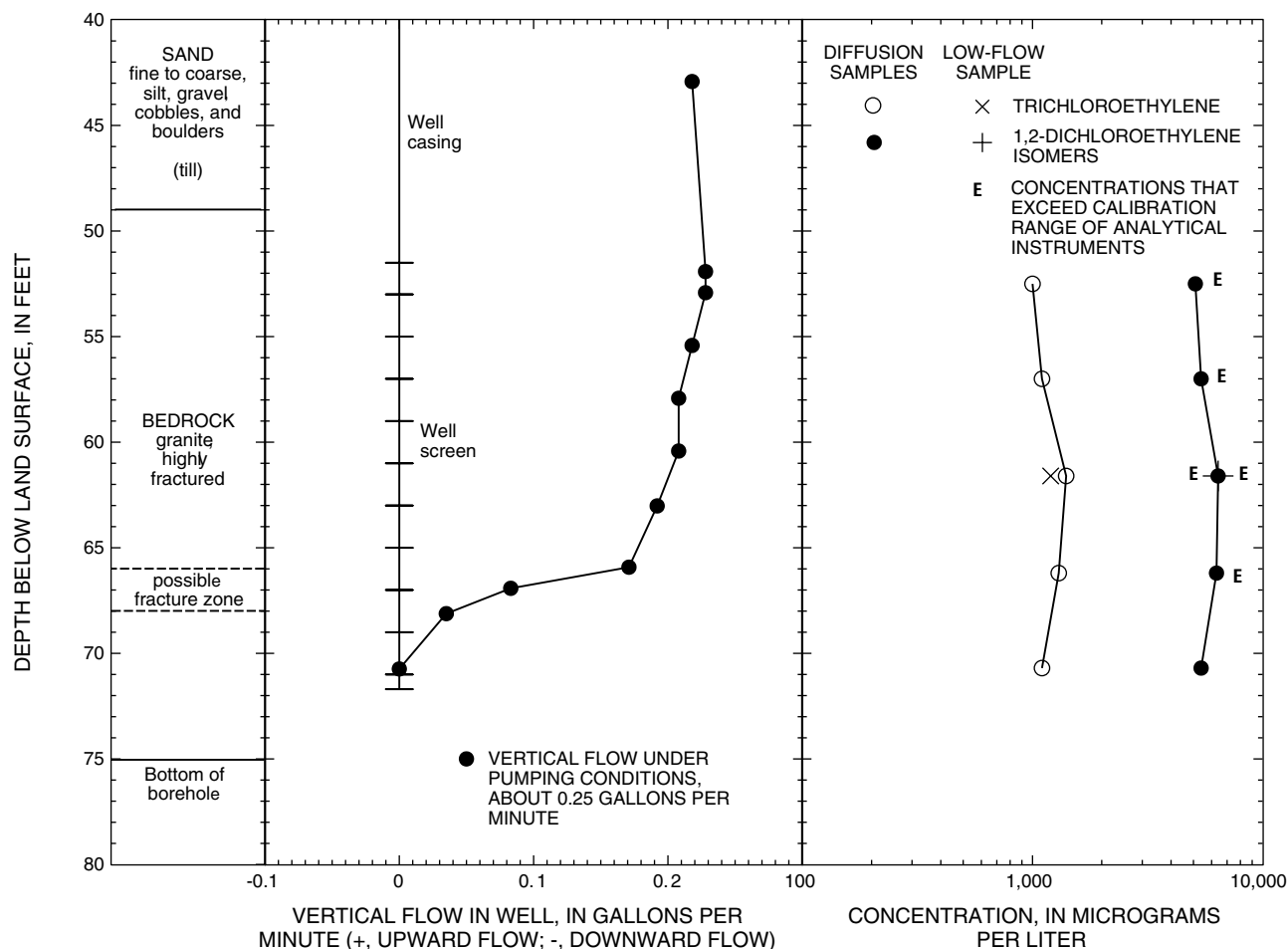


Figure 7. Lithology, well casing and screen, borehole-flowmeter data, and concentrations of 1,2-dichloroethylene isomers and trichloroethylene in multiple diffusion samples and in the low-flow sample at well RAP1-6R in the bedrock aquifer at Hanscom Air Force Base, Bedford, Massachusetts.

entering the upper part of the screen from a source in the upper bedrock or lower part of the till, or upward flow originating from the fracture identified or from fractures at depths below the well screen. It also is possible that this nearly uniform distribution of concentrations with depth in the screen reflects the distribution in the formation.

Concentrations of 1,2-DCE in the low-flow sample (also estimated above the calibration range) and in the midpoint diffusion sample appear to be the same, and the TCE concentrations from both methods are similar (fig. 7). The respective relative percent difference for concentrations of TCE is 15 percent. Although the entry point, or zone, of these waters is uncertain, both the diffusion and low-flow samples appear to be from the same source.

At well PO2-2R (30-ft well screen) (fig. 8), the large relative variations in concentrations of 1,2-DCE and TCE compared to those in samples from the other wells examined at this base (fig. 4) appear to result from the well screen intersecting a fracture or fracture zone. Although reliable ambient flow data were not obtained, borehole flowmeter data under pumping conditions indicate that most of the water pumped to the surface is contributed from a zone at and below a previously defined fracture (Tom Best, Restoration Program Manager, Hanscom Air Force Base, written commun., 1999). The depth to the top of this fracture, or fracture zone, was reported as 116 ft below land surface, but its downward extent was not provided in the drillers log. No flow was measured in the bottom 8 ft of the well screen, and little to

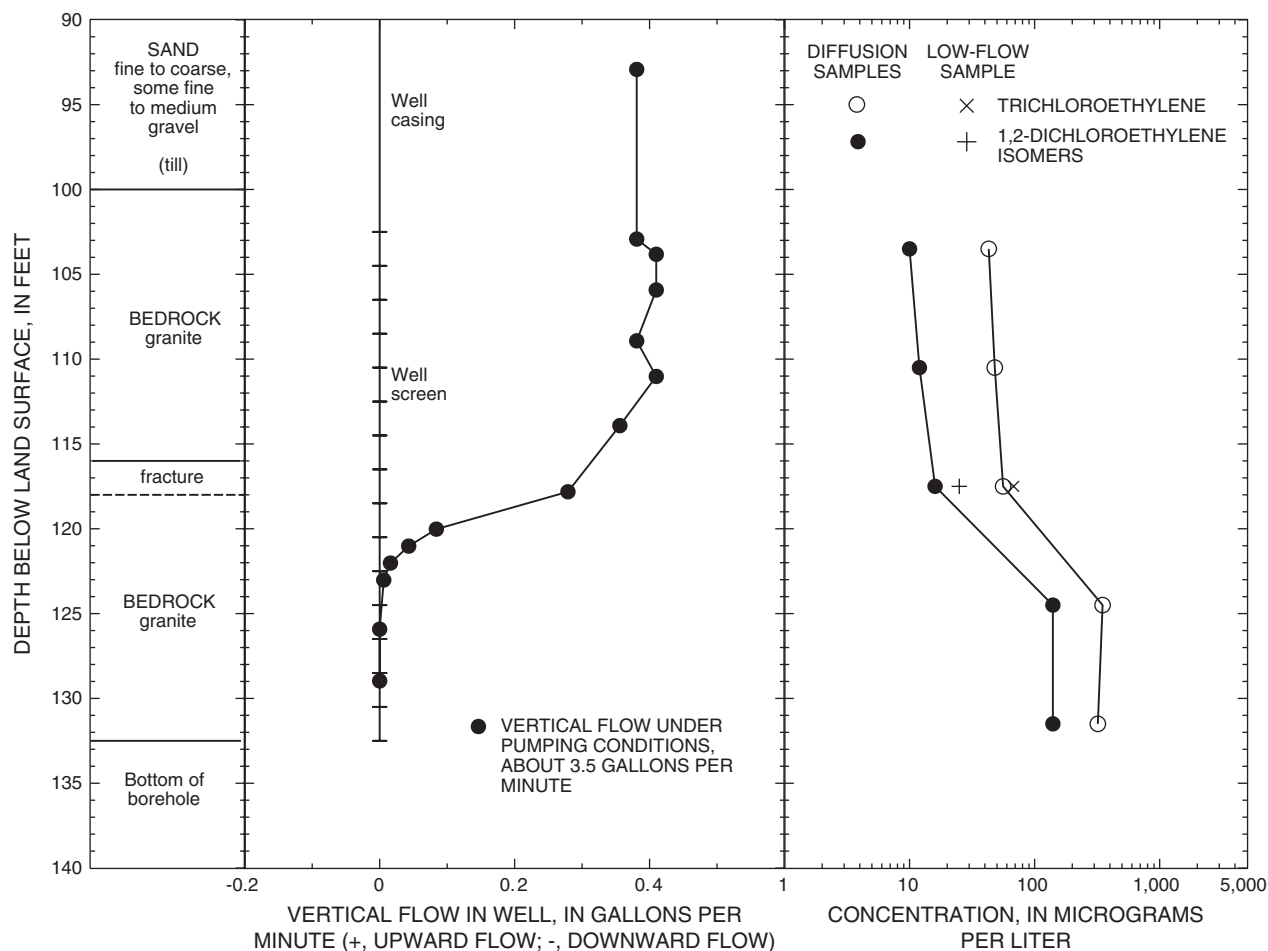


Figure 8. Lithology, well casing and screen, borehole-flowmeter data, and concentrations of 1,2-dichloroethylene isomers and trichloroethylene in multiple diffusion samples and in the low-flow sample at well PO2-2R in the bedrock aquifer at Hanscom Air Force Base, Bedford, Massachusetts.

no flow was measured in the upper 10 ft of the well screen. Therefore, this fracture, or fracture zone, may extend 5 or 6 ft below its reported upper level and account for the differences in concentrations above and below this zone. Although concentrations differ, nearly uniform distributions of 1,2-DCE and TCE concentrations are present above and below the fracture zone. This distribution of concentrations could reflect concentrations in the formation, however, other explanations are possible. Water in the zone below the fracture appears to be stagnant because no water was contributed to the flow while the well was pumped. Therefore, the lower concentrations above the fracture could represent temporal concentration changes that were not propagated into the zone below the fracture. The nearly uniform distribution of contaminants in the well screen

above the fracture could result from downward flow of contaminants from above into the fracture or upward flow from the fracture.

The relative difference between 1,2-DCE concentrations from the midpoint diffusion sample and the low-flow sample at well PO2-2R is 44 percent and for TCE concentrations is 19 percent. These differences in concentrations between methods, however, are much smaller than the differences in diffusion sample concentrations above and below the fracture. The relative difference of 1,2-DCE concentrations from above and below the fracture is about 170 percent and for TCE concentrations is about 150 percent. Similar to the other wells examined, the entry point(s), or zone(s), of these waters into the well screen is uncertain, however, both the diffusion and low-flow method appear to be sampling water from the same source.

SUMMARY AND CONCLUSIONS

This study has compared a diffusion sampling method to a low-flow sampling method for monitoring VOCs in ground water at the Hanscom Air Force Base, Bedford, Mass. In addition, the possible effects of vertical variations of VOCs and borehole flow in long-screen wells on sampling with diffusion and low-flow methods were examined.

Diffusion samplers have been shown to be a viable alternative to the low-flow sampling method currently being used at Hanscom AFB for monitoring VOCs in ground water. Concentrations of 1,2-DCE and TCE in samples collected at the midpoint of well screens with the diffusion sampling method were compared with concentrations of 1,2-DCE and TCE in samples collected at the same depths in wells with the low-flow sampling method. Concentrations of 1,2-DCE range from 8.2 to 2,500 µg/L in diffusion samples and 5.9 to 2,600 µg/L in low-flow samples. Concentrations of TCE range from 12 to 4,900 µg/L in diffusion samples and 11 to 4,900 µg/L in low-flow samples. A Sign test, applicable to these highly skewed concentrations, indicates that with a probability of 95 percent, it is equally likely to have diffusion sample concentrations of 1,2-DCE and TCE greater than low-flow sample concentrations as it is to have diffusion sample concentrations of 1,2-DCE and TCE less than low-flow sample concentrations.

Analysis of the distribution of 1,2-DCE and TCE concentrations in long-screen wells (screen length 10 ft or greater) in a till aquifer composed of a wide range of particle sizes from silt to boulders and in a bedrock aquifer with multiple diffusion samplers demonstrated that variations in concentrations within well screens differ significantly from well to well at the base. The vertical distribution of these concentrations in the long-screen wells may reflect the distribution of concentrations in the aquifer adjacent to the well screens. Borehole flowmeter data, however, indicate that the distribution of concentrations in samples from wells with long screens may be substantially affected by ambient vertical borehole flow.

In cases where there is either downward or upward borehole flow throughout most of the well screen, the concentrations of VOCs in the water that enter the screen are likely to predominate throughout the screen length as water(s) of different concentrations from other depths may be prevented from entering the screen. Analytical results from a single low-flow

sample should be similar to the analytical results from a single diffusion sample obtained from almost anywhere in the screen. Concentrations of VOCs in the well may be adequately characterized with both methods, however, the results may not be representative of the VOCs in the aquifer adjacent to the screen. Where vertical borehole flow is not present, VOCs in the well and aquifer adjacent to the screen may be adequately characterized with both methods at any specific depth. Delineation of the vertical distribution of VOCs with multiple diffusion samples may be needed, however, to determine an optimal depth for sampling with the low-flow method. If concentrations vary substantially with depth, however, an optimal depth may not exist and a single low-flow sample from any depth within the screen may not adequately characterize the VOCs in the well or the VOCs in the aquifer adjacent to the well. In a situation where borehole flow varies along the length of the screen, multiple diffusion samples may be able to characterize the vertical variations of VOCs in the well, but this depth profile may not represent the distribution of VOCs in the aquifer.

These observations reinforce results from previous studies that have demonstrated the difficulty of collecting representative ground-water samples in wells completed with long screens (Reilly and others, 1989; Church and Granato, 1996; Reilly and LeBlanc, 1998). A single sample collected with any method may not be representative of the formation water. Use of multiple diffusion samplers in conjunction with borehole flowmeter logs in long-screen wells may be useful in defining the vertical distribution of VOCs in the screened interval of an aquifer and evaluating if meaningful water-quality data can be obtained.

Other advantages of the diffusion sampling method over low-flow sampling methods include less overall time for collection of samples, no need for monitoring stabilization parameters to signal when sampling may begin, and minimal waste water. In addition, diffusion samplers have a distinct advantage over low-flow methods in evaluating the distribution of VOCs in wells because multiple samples can be obtained with minimal additional time over the time needed for collection of one sample. Multiple diffusion sampling in a well also can be effective even if diffusion samples are used only to select a location along the well screen where a sample should be taken with another method.

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Technology Application Analysis Report:
McClellan Air Force Base Environmental Management,
Sacramento, California

By McClellan Air Force Base Environmental Management Directorate

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McClellan Air Force Base Environmental Management,
Sacramento, California

The Technology Application Analysis Report summarizes the findings of a field demonstration using passive diffusion membrane samplers as an innovative approach to monitoring volatile organic compound (VOC) contamination in groundwater. The main objective of the demonstration was to compare the cost and performance of the diffusion samplers to conventional groundwater purge-and-sample techniques. The demonstration was conducted at McClellan AFB from May 12 to June 4, 1999, using 188 diffusion samplers in 30 groundwater monitoring wells contaminated with VOCs. The saturated screen length was 8 ft in one well, 10 ft in 17 wells, and between 10 and 20 ft in 12 wells. The tested compounds were trichloroethene; tetrachloroethene; 1,1-dichloroethane; 1,2-dichloroethane; 1,1-dichloroethene; *cis*-1,2-dichloroethene; carbon tetrachloride; chloroform; and Freon 113.

Statistical analysis of the demonstration data showed that the diffusion samplers produced sample results comparable to the results from conventional purge-and-sample samples. A cost comparison showed that diffusion sampling has the potential to dramatically reduce the costs associated with long-term monitoring.

Multiple diffusion samplers deployed along the length of the well screen showed significant vertical concentration variations in nine of the tested wells. The results implied that conventional sampling may not accurately represent the contaminant concentrations at points along the well screen because of mixing and preferential flow through coarse formations. The vertical contaminant concentration gradients shown by the diffusion samplers implied that the diffusion-sampler results were more representative of formation concentrations adjacent to the well screen than were the conventional-sampling results. The report concluded that for wells exhibiting vertical concentration gradients, guidance for optimal placement of the diffusion samplers along the length of the well screen still needs to be developed because placing a single diffusion sampler without knowledge of contaminant concentration gradients within the well could result in differences between conventional purge-and-sample and diffusion-sample results. The report also concluded that these diffusion samplers may only be appropriate for monitoring wells with hydraulic gradients sufficient to allow water within the well casing to exchange with formation water without purging.

The demonstration was conducted under the guidance of the Strategic Environmental Research and Development Program (SERDP) National Environmental Technology Test Site (NETTS) program at McClellan AFB.



VROBLESKY

USER'S GUIDE FOR POLYETHYLENE-BASED PASSIVE DIFFUSION BAG SAMPLERS TO OBTAIN VOLATILE ORGANIC
COMPOUND CONCENTRATIONS IN WELLS

PART 2: FIELD TESTS

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